THE FLOTATION OF MARGINAL GIBBSITIC BAUXITE ORES FROM PARAGOMINAS – BRAZIL

by

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STATEMENT OF THESIS APPROVAL

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ABSTRACT

Bauxite ore is the primary mineral resource for the production of aluminum metal and includes gibbsite [$Al(OH)_3$], diaspore [α-AlO(OH)] and boehmite [γ-AlO(OH)]. Gangue minerals generally include iron oxides (Hematite [Fe_2O_3], Goethite [FeO(OH)]), silicates (quartz [SiO_2]), kaolinite [$Al_2Si_2O_5(OH)_4$] and others such as rutile/anatase [TiO_2]. Samples from the Paragominas deposit, Brazil, were received for the thesis research including a high grade marginal ore (BNC) and a low grade marginal ore (BN).

Current plant recoveries in the processing of the higher grade bauxite ore have been on the average of 25% when treated by grinding and desliming but these high grade reserves are being depleted. The utilization of marginal quality bauxite ores has been considered and flotation technology for treating BNCs and BNs were studied. Ore characterization indicates that gibbsite is the major aluminum mineral while kaolinite is the predominant silica gangue mineral. Bench flotation tests using customized collectors were evaluated directly for the ground material and after desliming. Both direct and reverse flotation strategies were considered for the flotation of the marginal bauxite ores, BN and BNC.

Liberation analysis revealed that kaolinite is not so well liberated especially for the low grade marginal ore, BN. In contrast, the aluminum oxide mineral (gibbsite) presents a higher liberation degree. Results carried out by QEMSCAN indicated that more than 50% of the gibbsite is found in minus 106 micron particles

containing more than 70% gibbsite. Only 8% of the kaolinite is found in minus 106 micron particles containing more than 70% kaolinite.

Results from the reverse flotation of kaolinite were found to be satisfactory without desliming using a customized amine-fatty acid as collector, sodium hexametaphosphate (SHMP) as dispersant, and starch as depressant at pH < 6.0. Concentrates containing Al_2O_3 to SiO_2 ratios of 7.41 and 9.83 were obtained with an Al_2O_3 recovery of 55.9% and 70.9% for the BN and BNC bauxite ores respectively. On the other hand, direct flotation of gibbsite from the bauxite ore was accomplished with desliming at pH 10.5 using an alkyl hydroxamate-fatty acid as collector, sodium carbonate as dispersant, and sodium silicate as depressant. Concentrates with Al_2O_3 to SiO_2 ratios of 8.44 and 10.58 were produced with an Al_2O_3 recovery of 32.0% and 64.5% for the BN and BNC ores respectively.

The research reported in this thesis, one of few reports on the evaluation of flotation for the concentration of marginal quality gibbsitic bauxite ores, gives evidence for the successful treatment of marginal gibbsitic bauxite ores. Further discussion on pH effect, particle size, and flotation reagents on the flotation response for both BN and BNC ores are discussed.

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CHAPTER 1

INTRODUCTION

1.1 Bauxite Ores

Bauxite is the principal ore for the production of aluminum metal, nonmetal products and nonmetallurgical applications with aluminum such as refractories and abrasive materials (Meyer, 2004). The production of aluminum metal is generally accomplished by the Bayer process, which is a wet chemical, caustic leach process, forming alumina, followed by the Hall-Héroult process, a fused salt electrolytic reduction of alumina to aluminum metal. The efficiency of production depends upon certain variables such as available alumina, reactive silica, impurities, and mineralogy. Thus, the efficiency of aluminum production varies with the bauxite characteristics of the feed material. Generally, high grade bauxite ore is directly fed to the Bayer process, but these high grade resources are being depleted. Low grade bauxite resources may require processing either by particle size separation or flotation in order to prepare a material suitable for feeding the Bayer process. The quality of bauxite ore feeding the Bayer process is measured by the "available alumina" and the "reactive silica" but it can also be defined by the Al_2O_3 to SiO_2 weight ratio, which has to be higher than 10 to be considered as high grade bauxite ore.

These are two major types of bauxite, "lateritic" and "karst" bauxites, with both being weathered products from underlying parent rock. Lateritic bauxites are derived

from primary aluminosilicate rocks, whereas karst bauxites are derived from interbedded carbonate and aluminosilicate rocks (Smith, 2009). Lateritic bauxites are formed in equatorial regions and, represent approximately 90% of the world's exploitable bauxite reserves (Freyssinet et al., 2005). As a consequence of the weathering process, the valuable aluminous material (generally gibbsite), lies on top of an aluminosilicate base which is often clay. Karst bauxites have the presence of carbonates in the parent rock. Silicate minerals are also dominated by kaolinite but may include more difficult to process minerals. Other aluminous minerals are more likely to be diaspore as found in Eastern Europe, India and China.

The world bauxite production in 2010 reached more than 200 million tons according to the United States Geological Survey, USGS (Bray, 2011). Australia leads the ranking with 70 million tons**,** followed by China and Brazil with 40 and 32 million tons respectively. The production growth rate over the last four years has been**,** on average**,** 5% per year. The most significant reserves are located in Guinea (26.4%), Australia (19.2%), Brazil (12.1%) and Jamaica (7.1%) as indicated in the report prepared by Bray (2011). These reserves are defined based on the feed required for treating the bauxite ores by the Bayer process and subsequent treatment of alumina by the Hall-Héroult process. In Brazil, the fourth largest alumina producer, most of the aluminum and its products are used in the packaging and transportation industries followed by electric power and civil construction industries and represent 1% of Brazil's total GDP. Approximately 98% of the bauxite produced in Brazil is used for alumina production while the other 2% goes to the refractory industry as well as to the chemical industry.

1.2 Brazilian Bauxite Scenario

Currently high grade bauxite processing generally consists of size reduction and separation of aluminum minerals from silicate gangues through a wet screening process. This process is effective in reducing the silica content in the bauxite if the silica is preferentially concentrated into smaller particle size fractions, or fines (Smith, 2009). Prior to size reduction, selective mining is carried out and consists of identifying and mining specific areas of desirable quality in the deposit. As a result of this strategy, a significant amount of marginal quality bauxite ore is not processed and the potential of the ore body is correspondingly reduced.

The Brazilian aluminum business has grown significantly with the discoveries of new deposits and recently with the start-up of the Paragominas beneficiation plant in 2007. In Brazil, there are two main areas containing bauxite ore but each with different mineralogy. One is located in the north region of the country (State of Pará) and the other in the central-south region (State of Minas Gerais). While more than 85% of the total Brazilian production comes from the north region, the central-south region is also looking forward to expanding plant capacity (IBRAM, 2011). Table 1.1 exhibits the current production and alumina grade for both Pará and Minas Gerais States. Although the north region contains high-grade aluminum deposits, the central-south region provides better access to infrastructure enabling the installation of processing plants and the distribution of the product. Besides the high alumina content, the bauxite from the north region contains mostly kaolinite as the silica mineral, while the deposits from the central-south region contain both kaolinite and quartz.. The production in Pará, the north region, reached over 25 million tons with a run-of-mine containing 50 - 53% alumina on average.

Table 1.1 Brazilian bauxite deposits with corresponding year production and alumina grade (Bray, 2011).

	Pará		**Minas Gerais**	
	Trombetas	**Paragominas**	**Poços de Caldas**	**Cataguases**
ROM[§] Million tons	19.6	8.7	2.3	2.4
Alumina, %	55.0	55.0	45.0	45.0

§ Run of mine

The current practice at these plants is to remove the fine clay minerals, after crushing and grinding. The ground product is then classified in hydrocyclones to remove fine particles less than 150 microns which includes the clay minerals. The overall metallurgical recovery is in the range of 30-40%. A similar recovery is observed in the central-south region where 5 million tons are produced from an ore containing approximately 45% alumina processed through scrubbing, crushing and desliming in hydrocyclones.

1.3 Flotation of Bauxite Ores

Flotation technology is used extensively in mineral processing plants, especially for the treatment of low grade ores. The high separation selectivity and the significant processing capacity make flotation the most widely used technology for the concentration of ores. Flotation can be applied in bauxite ores either by removing the impurities (reverse flotation) or by floating the valuable minerals (direct flotation).

Extensive research has been done in China to upgrade the diasporic bauxite ore, generally lower grade, through flotation. The first Chinese plant for bauxite beneficiation by flotation was installed in Zhongzhou, Henan Province. The ore contains 65% diaspore as the primary bauxite mineral with kaolinite, illite and pyrophyllite as the gangue silicate minerals. A grinding circuit with cyclones reduces the ore size and eliminates fines smaller than 45 microns which corresponds to 3.5% of the feed mass. The cyclone underflow is sent to flotation which includes one rougher, two scavengers and two cleaner stages. The plant has a mass recovery of 78.8% and an aluminum recovery in the concentrate of 84.9% with respect to the flotation feed and with a ratio of alumina to silica greater than 11 (Zhao et al., 2010).

The application of flotation to the concentration of bauxite ore is dependent on the understanding of surface properties of the minerals to be separated. Independent of the bauxite type, the silicate minerals are mainly kaolinite and quartz. While the flotation of quartz is quite well understood in reverse flotation systems, the flotation of kaolinite is under extensive investigation and recently its surface characteristics under different solution conditions have been studied (Gupta, 2011). In the case of direct flotation (gibbsite and diaspore) some attention has been received by researchers but a lack of publications on this topic is evident, especially for the case of gibbsitic bauxite ores.

1.4 Current Bauxite Processing Technology

The Paragominas plant in Brazil was designed to treat 15 million tons of high quality bauxite per year, which is found 20 meters deep into the ore body. The top layer consists mostly of clays and is discarded as overburden while the middle layer, consisting of three levels of marginal ore, should be considered for feeding the plant and increasing the life expectancy of Paragominas deposit. The bottom layer, rich in available alumina, is the major source for the current processing but its resources are being depleted. In order to increase the life expectancy of the plant, the combination of the marginal ore from the middle layer with the rich ore at the bottom layer is been considered and research has been initiated in this thesis investigation. The strategy is to evaluate the possibility for treating this combined ore by feeding flotation with the cyclones underflow after first desliming at 45 microns. The current flow sheet for the Paragominas plant consists of a primary roll crusher which reduces the ore size to 200-150mm.

After crushing, the ore goes to a homogenizing pile and feeds the semi-autogenous grinding circuit. The plus 12 mm size is sent to the impact crusher and then to

the ball mill while the screen undersize is classified in hydrocyclones 26 inches in diameter. The desliming occurs in two stages called fine desliming (45 microns) and ultrafine desliming (15 microns). The product size is within 150 and 300 microns. The overall mass recovery is around 60% and the metallurgical recovery of alumina is about 40% from mine feed to the product according to Paragominas plant data. After particle size separation by cyclones, no further processing is performed with the ore and the final product is ready to be processed through the Bayer process.

The bauxite concentrate from the crushing, grinding and desliming plant is prepared for aluminum production using the Bayer process, which consists of bauxite concentrate digestion with sodium hydroxide (NaOH) at 175^{o}C to produce alumina. The other components, iron oxide and silicates do not dissolve significantly and are filtered forming a solid impurities by-product, called *red mud*. The caustic aluminum hydroxide solution from the Bayer Process is then cooled and the dissolved aluminum precipitates. The precipitate is heated to 980^{o}C and the aluminum hydroxide decomposes to alumina, with the release of water. The quality of bauxite concentrate plays an important role in the efficiency of the Bayer process especially concerning the silica content present in the concentrate. As the silica content increases, the temperature required for digestion also increases.

1.5 Research Objective

In order to achieve the desired quality when treating marginal bauxite ores, different flotation strategies were evaluated with respect to collector, dispersant, depressant, pH and particle size. The present research determined the liberation characteristics of the aluminum and silicate minerals for two types of gibbsitic bauxite

ores of marginal quality, and established a flotation reagent schedule for the flotation of gibbsite (direct flotation) and the flotation of kaolinite (reverse flotation). An important aspect of the research was to identify a satisfactory reagent schedule to achieve the desired concentrate quality. The effect of desliming prior to flotation was also considered and compared to flotation without desliming using appropriate reagents for fine particle flotation.

CHAPTER 2

LITERATURE REVIEW

The flotation chemistry of nonsulfide minerals differs from sulfide mineral flotation in many aspects. In general, nonsulfide minerals are hydrophilic and require relatively high levels of collectors (on the order of 500 – 1500 g /t) to establish a hydrophobic surface state. The collectors used in nonsulfide flotation generally are cationic or anionic surfactants, with hydrocarbon chains of 10 carbon atoms or greater resulting, sometimes, in insufficient solubility and consequently, a distinct collector phase is present in the system as a liquid dispersion or as a collector colloid (Miller et al., 2007, a).

Nonsulfide flotation also differs technically from sulfide flotation technology with respect to particle size. In the case of nonsulfide systems, flotation is accomplished after desliming the feed (i.e., iron ore, phosphate and potash) or in some cases involves flotation of micron-size particles (i.e., taconite and kaolin). With respect to flotation rate, longer retention times are required for the flotation of impurities, like anatase from kaolin, while rapid flotation is accomplished in phosphate flotation (Miller et al., 2007, a). Flotation technology has been extensively applied for the separation of valuable minerals from gangue minerals. The flotation efficiency is dependent on the characteristics of surface-active species that adsorb at the mineral surface and their capability to make the selected mineral hydrophobic by adsorption or association of

collector with them (Somasundaran and Ananthapadmanabhan, 1987). Also important are the physical aspects of flotation systems which play a major role in the flotation process including bubble size and mineral particle size (Reay and Ratcliff, 1975).

2.1 Fine Particle Flotation

Following the initial theory of flotation proposed by Gaudin et al. (1942), Derjaguin and Dukhin (1961) published research dealing with the flotation theory for small and medium-size particles. According to them, the overall rate probability for flotation (E) is dependent on the probability, or efficiencies, of bubble-particle collision, attachment and stability (or detachment) as shown in equation 1. It is well known that fine particles exhibit different behavior than large particles during flotation, especially with regard to their low flotation rates. One of the reasons for this inefficiency during flotation of fine particles is related to the low probability of collision in conventional flotation systems with bubbles of a given size and velocity (Fuerstenau, 1980). Recently, efforts have been made to increase bubble-particle collision efficiency (Ec) either by decreasing bubble size or by increasing apparent particle size and promising results was achieved when nano-bubbles were used (Miettinen et al., 2010).

$$E = Ec * Ea * Es \quad (1)$$

The probability of attachment (Ea) is defined by hydrodynamics (induction time) and equilibrium state (contact angle measurements) (Miettinen et al., 2010). The induction time is the time required for the rupture of the water-film at the interface and subsequent attachment of particle to bubble. It is intuitive that induction time varies with

particle diameter and several studies have tried to establish a correlation between them but without much practical applicability (Sutherland, 1948; Trahar and Warren, 1976).

When the three-phase contact line between a bubble, particle and solution is formed, a very strong force is necessary to break it and the equilibrium situation among them is called stability. This force could be inertia, gravity or viscous forces and it increases with increasing particle size, for the mass of the particle and for the area exposed to the detaching fluid flow (Miettinen et al., 2010). The detachment force was estimated to be a million times greater for a particle size of 100 microns than for a 1 micron particle (Ye and Miller, 1988). For fine particle flotation, the bubble-particle stability (Es) can be considered stable if they form a three-phase contact line with a bubble even in a turbulent environment.

Now bubble-particle collision mechanisms are better described in the literature and several models involving the factors affecting bubble-particle collision are available. The forces that make the particle deviate from its trajectory from fluid streamlines near the bubble surface and interact with a bubble include gravitational forces, inertial forces and hydrodynamic drag forces. Bubble-particle collision by diffusion has also been defined. Various parameters affect bubble-particle collision including mineral particle size and density, bubble size, bubble rising velocity and bubble surface mobility. For submicron particles, where Brownian motion is the major collision mechanism, the bubble-particle collision efficiency has been found to increase with decreasing particle and bubble size (Derjaguin et al., 1984; Nguyen et al., 2006).

Fine particles, such as kaolinite, fall into this category and their flotation behavior has been studied in more detail recently with respect to the processing of bauxite ores.

Thus the aggregation of fine particles, which is one of the alternatives for overcoming this problem, lacks the desired selectivity and applicability in flotation systems is restricted (Miettinen et al., 2010).

It is also important to mention that fine particles possess a high surface area and a higher collector dosage is expected. Klimpel (1980) has found that as the collector dosage increases, the flotation rate for large size particles increases, the rate for medium size particles remains constant while for fine particles, the flotation rate decreases. One possible explanation is that the collector concentration changes the bubble attachment time and that has more impact on coarse particles by changing the probability of attachment. Fines are generally characterized by small mass and large specific surface area requiring different treatment compared with coarser particles (Klimpel, 1980; Ramachandra, 2004).

As particles become finer, at the colloidal size range for example, the effect of long range intermolecular forces and electrical double layer forces become significant and tend to control the particle-particle interaction. If the double layer is thick and potentials are large and of the same sign for two minerals, the particles remain dispersed but if the double layer is thin or absent, attractive forces dominate and particles aggregate. If the aggregates formed are hydrophobic, they will attach to the air bubble leading to low selectivity. If the two minerals have an opposite surface charge the electrostatic attraction leads to slime coating of one mineral onto another (Klimpel, 1980). This phenomenon can be controlled by adjusting the system potential. In the case of bauxite flotation, the fine particles are generally formed by clays and a small amount of other minerals.

A research study carried out by Fuerstenau (1980) comparing the effect of slimes on flotation behavior shows that chemisorbing collectors are not affected by the presence of slimes while with physically adsorbing collectors, which is probably the case during the reverse flotation of kaolinite by amines, slimes have a negative effect. The research was done using hematite in a conventional system with an anionic sulfonate collector, which functions by electrostatic adsorption. By replacing the sulfonate used as collector by octyl hydroxamate, Fuerstenau et al. (1970) obtained high recoveries. It was stated that the strength of the chemisorption adsorption reaction resulting from specific chemical interaction between the hydroxamate and hematite surfaces resulted in a strongly hydrophobic hematite, which offsets the electrical attraction between fine hematite and quartz.

2.2 Direct Flotation of Gibbsite from Bauxite Ore

Generally, gibbsitic bauxite ores have significantly higher alumina concentrations than diasporic bauxite ores but publications of research involving its processing are quite rare. One probable reason is that the high grade deposits currently used do not require special treatment to achieve the desired grade for the Bayer process but as the necessity for treating lower grade bauxite ores arises and higher recoveries are expected, flotation technology must be considered.

Bittencourt (1989) studied the flotation of a gibbsitic bauxite ore containing quartz. The strategy developed was to float gibbsite and kaolinite first from quartz at pH 2.0 with 20% solids using sodium dodecyl sulfate (SDES). After that, for the flotation of kaolinite from gibbsite, cetyltrimethylammonium chloride was used as collector at pH 6.0 and 20% solids. A final alumina recovery was estimated to be 60% considering desliming

at 3 microns prior to flotation. A concentrate with 64.7% Al_2O_3 (97.4% calcined basis) was produced for use in the refractory industry.

The flotation of gibbsite was also studied by Balashova and Kuznetov (1970) using oleic acid as collector and sodium hexametaphosphate (SHMP) as depressant for kaolinite. Bittencourt (1989) subsequently performed tests evaluating the effect of sodium hexametaphosphate (SHMP) and it was shown that depression is effective but with very low selectivity since the Al_2O_3 recoveries dropped significantly in an alkaline condition (pH 9.0). When SDES with SHMP was used at pH 2.0, similar behavior occurred with no variation in Al_2O_3 grade. It is expected that higher recovery could be obtained at pH higher than pH 9.0 since the PZC of the gibbsite generally occurs at about pH 6.2 to pH 9.2 depending on the sample aging preparation (Gupta, 2011; Parks, 1965).

For effective flotation of bauxite, the use of depressants and dispersants also has to be considered. The effect of sodium carbonate on the dispersion of diaspore and kaolinite was investigated by Wang et al. (2007). Experiments were conducted to analyze the effect of pH and Na_2CO_3 concentration on the dispersion of diaspore and kaolinite using particles less than 38 microns during the sedimentation process. Apparently, both minerals tend to be agglomerated in acidic solution (pH < 4.0) and dispersed in alkaline solution (pH > 9.0). It was demonstrated by zeta potential measurements that the negative zeta potentials of the minerals increased with the addition of Na_2CO_3 and the electrostatic repulsion between the mineral particles was also increased, improving the dispersion of aluminum and silicate minerals.

Bittencourt also studied the effect of depressants during his research, especially the effect of sodium silicate on the flotation of gibbsite and kaolinite from quartz. The

addition of 100 g /t of sodium silicate in the rougher and cleaner stages increased the silica grade in the tailings and increased the alumina grade in the concentrate. The depression of silicate minerals was effective until a certain limit when no more variation was observed on grade and recovery. The gibbsite pH is found to be between the range of pH 6.2 and pH 9.0 depending on the sample preparation procedure, origin and aging (Gan and Franks, 2006).

2.3 Reverse Flotation of Kaolinite from Bauxite Ore

The flotation chemistry fundamentals for aluminosilicate minerals were reviewed by Fuerstenau and Raghavan (1978). Basically, the aluminosilicate minerals consist of silica tetrahedra and alumina octahedra organized in different structures that distinguish one aluminosilicate mineral from another. Because of the similarity in size between aluminum, Al^{3+}, and silicon, Si^{4+}, the substitution of Si^{4+} by Al^{3+}, or the substitution of Al^{3+} by Fe^{2+}/Mg^{2+} influences the aluminosilicate mineral structure. Since the aluminosilicate minerals are composed of a mixture of Al-O and Si-O bonds, the surface properties of cleaved aluminosilicate particles are determined by the exposure of Si-O and Al-O sites and their physicochemical properties. The Si-O and Al-O chemical bonds in aluminosilicate minerals have both covalent and ionic bonding characteristics (Fuerstenau and Raghavan, 1978). Further review of the surface chemistry of layered silicate minerals has shown their anisotropic characteristics and the expected complexity of their behavior in flotation systems (Miller et al., 2007, b).

The flotation of kaolinite from diasporic bauxite ores has been extensively studied in the last 10 years, especially by Chinese researchers (Yu et al., 2008; Xu et al., 2004; Qin et al., 2003; Hu et al., 2003, a). It has been shown that reverse flotation, or flotation

of kaolinite, exhibits some advantages over the direct flotation of diaspore including lower cost due to lower collector dosages, easier dewatering due to the cationic collectors used and less effect on the Bayer process (Liu and Liu, 2005).

Reverse flotation should be suitable for the beneficiation of low grade bauxite ores; however, there are several difficulties associated with the presence of slimes, particles less than 0.01 mm. The need to find or design an effective collector for silicate and an effective depressant for alumina minerals is obvious. Common reagents used for cationic reverse flotation have been fatty amines as collectors, sodium silicate and starch as dispersant/depressants and sulfuric acid and sodium carbonate as pH regulators. Recently developed collectors that have been found to be effective for the flotation of kaolinite, illite and pyrophyllite include N-(2-aminoethyl)-lauramide, N-(3-aminoethyl)-lauramide, N-alkyl-1, 3-propane diamine, alpha naphthylamine, 313 N, N-dimethyl-dodecyl amine (DRN) and Nn-decyl-1,2-diaminopropanes (DN12) as discussed by Yu et al. (2008).

The most common depressant for diaspore is sodium hexametaphosphate, SHMP, and flotation is accomplished in acidic conditions. Chen et al. (2005) studied the effect of SHMP on the flotation separation of kaolinite from diaspore. He explained that the interactions between the phosphate groups are due to the bridges formed among them with Al atoms of diaspore and kaolinite exposed on the surface. Adsorption measurements show that the adsorption is more effective on the surface of diaspore, reaching a maximum at pH 6.0. Using dodecyl-amine chloride, DDA, at $3x10^{-4}$ mol /L. Bittencourt (1989) also used SHMP to separate kaolinite from gibbsite at pH 9.0 and to float kaolinite from gibbsite at pH 2.0. The results indicate that at a high concentration of

SHMP, 300 g /t, flotation recovery of Al_2O_3 decreases significantly. Chen suggests that for high selectivity during flotation, high dosages are required. It is important to notice that Bittencourt used oleic acid for the flotation of gibbsite and sodium dodecyl sulfate for the flotation of kaolinite instead of an amine such as DDA.

Starch is an important natural polysaccharide and has been broadly applied in mineral processing as either a flocculant and/or depressant. Because of the presence of OH groups in their basic structural unit, D-glucose, starch molecules are hydrophilic. However, ordinary starch shows poor selectivity and depressing effect in the reverse flotation of aluminosilicates, such as kaolinite, from bauxite (Ma et al., 2009). Adsorption of starch on kaolinite surfaces was investigated recently by Ma and Bruckard (2010). It was shown that starch adsorption on kaolinite is significantly dependent on pH. By decreasing pH, the electrostatic repulsion between the anionic starch molecules and the negatively charged kaolinite particles (pH > 4) is reduced. At low pH, starch shows high affinity towards kaolinite and starts to play an important role in the flocculation and depression of kaolinite particles.

2.4 Surface Properties of Kaolinite

Kaolinite is a two-layer silicate mineral consisting of alternating layers of silica tetrahedral and aluminum hydroxide octahedral. It has been established that kaolinite has a heterogeneous surface charge among its basal planes and edges. The hydrogen bonding between the hydroxyl ions of one sheet with the tetrahedral oxygens of the next layer holds the structure together. The hydrogen bonds are weak, and consequently, kaolinite clay is a soft material (Hu and Liu, 2003).

The crystallographic structure suggests that kaolinite particles consist of a silica tetrahedral surface, (0 0 1 basal plane), and an aluminum hydroxide octahedral surface (0 0 $\underline{1}$ basal plane). Kaolinite particles also have (0 1 0) and (1 1 0) edge surfaces which are generated as a result of broken covalent bonds as shown in Figure 2.1 and consequently their surface charge densities will vary with solution pH. Recent studies from Gupta et al. (2011) revealed a distinct dependence of pH on the surface charge densities of the silica surface face and the alumina surface face of kaolinite particles, as determined by surface force measurements using atomic force microscopy (AFM) and traditional titration experiments (M-R titration and potentiometric titration). The assumption that both basal planes carry a fixed negative charge has only recently been examined through surface force measurements using atomic force microscopy. On the other hand, the edge surface shows pH dependence with respect to its surface charge.

These colloidal force measurements reveal that the silica tetrahedral face of kaolinite is positively charged at pH < 4.0, whereas the alumina octahedral face of kaolinite is positively charged at pH < 6.0 and negatively charged at pH > 8.0. These results suggest that the iso-electric point (IEP) of the silica tetrahedral face is at pH < 4.0 and the iso-electric point of the alumina octahedral face lies between pH 6.0 and 8.0 (Gupta and Miller, 2010). Both titration experiments and electrophoretic zeta potential measurements suggest an overall average point of zero charge of kaolinite particles close to pH 4.5.

Because of the difference and variation of the surface charge of kaolinite surfaces, particle interaction is also affected by pH. In a suspension of clay particles, there are three different modes of particle associations forming aggregate structures depending on

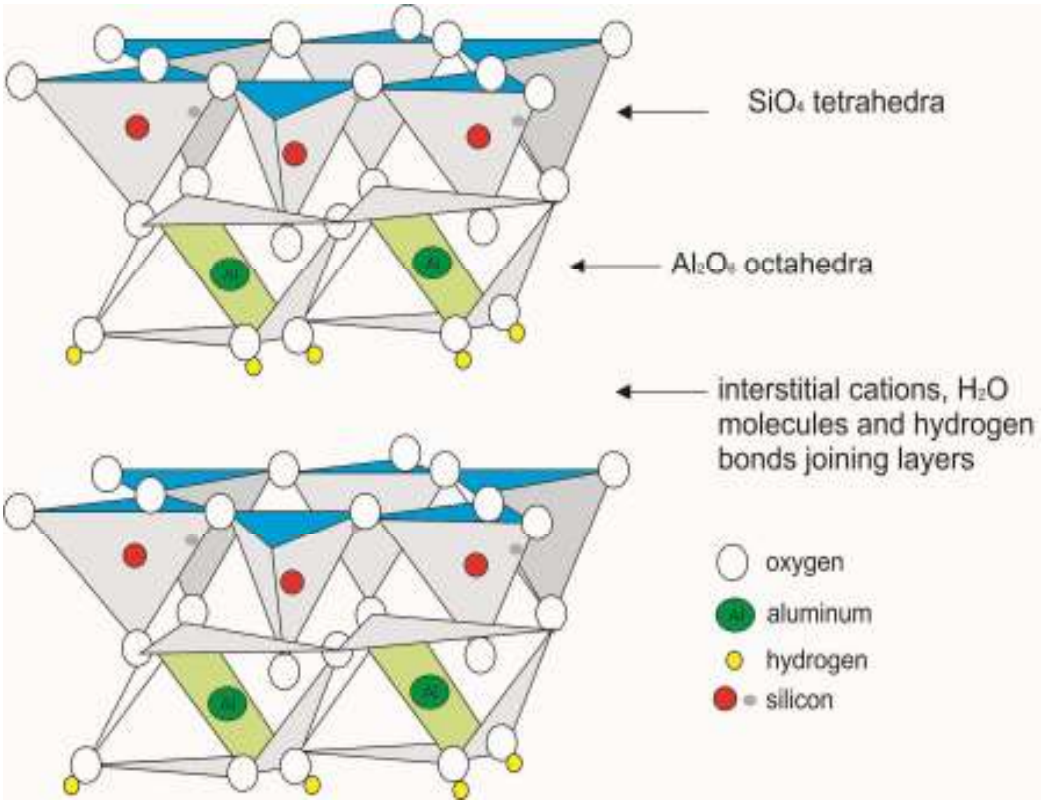

Figure 2.1 The structure of kaolinite showing a silica tetrahedral layer and an alumina octahedral layer along the basal and edge planes.

the surface charge: face-face, edge-face and edge-edge. The results indicate that face-face (silica face – alumina face) is the dominant particle interaction at low pH values, which promotes edge-face (edge silica and edge alumina face) and face-face (silica face-alumina face) interaction at intermediate pH values.

The formation of these aggregates at low pH due to face-face (silica face-alumina face) interaction presents a maximum shear yield stress and increases the stacking of kaolinite layers. Further analysis indicated the effect of aspect ratio (ratio of particle diameter to thickness) is significantly higher for the face-face interactions (silica face - alumina face) at pH 5.0 (Gupta, 2011).

2.5 Collector Adsorption by Kaolinite and Gibbsite

Researchers in Hu's group at Central South University, P.R. China (Chen et al, 2005; Wang et al, 2007; Hu et al, 2003, (b); Hu et al, 2005; Hu et al, 2003 (b); Hu et al, 2004) have made significant contributions toward the understanding of surfactant adsorption on aluminosilicate minerals, such as kaolinite, and the development of new and efficient collectors for the separation of aluminosilicate minerals from diasporic bauxite ores. Considering the point of zero charge, PZC, of kaolinite to be about pH 4 as shown in Figure 2.2, cationic collectors have been considered and developed for the removal of silica from bauxite by reverse flotation (Xu et al., 2004). It has been reported that Fourier Transform Infrared (FTIR) spectra show that the possible adsorption of cationic surfactants at the negatively charged surface of kaolinite particles is through electrostatic and/or hydrogen bonding (Zhao et al., 2010, Hu et al., 2005).

Studies on amine adsorption by kaolinite, revealed an important characteristic for flotation considerations (Hu et al., 2004). It was demonstrated that the 001 basal plane,

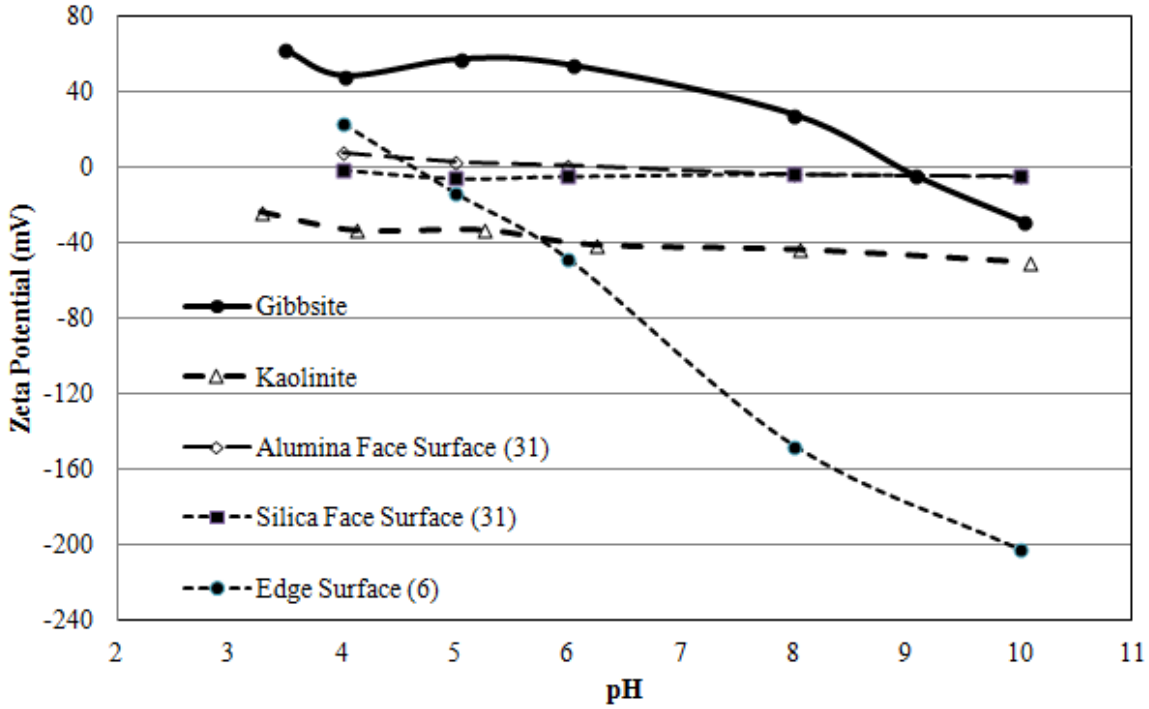

Figure 2.2 Electrokinetic behavior of kaolinite (Brindley, G.W., 1979), gibbsite (Gan and Franks, 2006), alumina face surface (Gupta and Miller, 2010), silica face surface (Gupta and Miller, 2010) and edge surface (Gupta, 2011) in 1mM-KCl measured by electrophoresis.

the silica tetrahedral layer, exhibits a strong affinity to cationic collectors due to the presence of oxygen atoms at the surface that make the 001 plane highly amenable to form H-bonds with species that have electron-acceptor characteristics. In contrast, the alumina octahedral layer, 00$\underline{1}$ plane, has a strong energy barrier preventing the amine molecules from approaching and leading to weak adsorption at this basal plane.

Consequently, the researchers developed a special reagent that promotes the aggregation of kaolinite particles through flocculation of the alumina octahedral layer, maximizing the exposure of the silica tetrahedral layer which can better adsorb the flocculant. This process was called "macromolecule enhanced kaolinite flotation." Based on Gupta and Miller (2010) and Gupta et al. (2011) results, it seems difficult to explain their proposed aggregation of kaolinite particles for maximum exposure of the silica face.

The use of alkyl hydroxamates in the flotation of minerals that chelate with hydroxamate is well known by the industry (Hu and Liu, 2003). Hydroxamates are powerful collectors in flotation due to their ability to selectively chelate at the surface of minerals that contain titanium, iron, and magnesium, among others. The hydroxamate collectors can be used effectively at pH > 6. Also, the hydroxamate collectors possess frothing properties so that frother addition is usually not required for flotation (Miller et al, 2007 (a)). The use of alkyl hydroxamate for the possible flotation of gibbsite has not been reported and will be considered in this thesis research program.

2.6 Summary

Efforts are now being made to develop improved flotation technology for the efficient processing of low grade bauxite ores. Such resources are classified according to the primary bauxite mineral (gibbsite, boehmite or diaspore) and according to gangue

minerals (quartz, clays, iron oxides, etc.). The flotation of two gibbsitic bauxite ores with and without desliming will be discussed with respect to flotation strategy, mineralogy, liberation characteristics and reagent schedule. Optimum flotation conditions are expected to happen in acidic conditions for the flotation of kaolinite considering the negatively charged kaolinite surfaces reacting with the positively charged amines (physisorption), while gibbsite remains positively charged, and in alkaline conditions for the flotation of gibbsite, assuming that the adsorption of the hydroxamate collector onto the gibbsite surface occurs by chemisorption. The effectiveness of both strategies, direct flotation and reverse flotation, has to be accomplished using the appropriate dispersant and depressant in order to achieve the specifications required by the Bayer process and with a satisfactory alumina recovery. While some researchers understand that the adsorption of amines by kaolinite happens through hydrogen bonding in acidic media, recent studies show that the difference in surface charge for the kaolinite surfaces results in an electrostatic attraction between kaolinite particles forming aggregates of an anisotropic character. Clearly further research study of collector adsorption by kaolinite is warranted.

CHAPTER 3

MATERIALS AND METHODS

3.1 Bauxite Samples

Bauxite samples were obtained from the Paragominas bauxite complex in northern Brazil, located 220km south of Belém, Para's capital, and 70 km southwest of Paragominas city. The mine is located in the Amazon sedimentary basin, and is characterized by a well-developed drainage system, forming low valleys that separate isolated plateaus. The Paragominas bauxite deposits are developed on a 10,000 km² plateau and the average altitude on the plateaus is not higher than 150 m (Silva et al., 2008). The Paragominas deposit is the world's third-largest bauxite complex.

The two main deposits of Paragominas currently being explored are designated "Miltônia 3" and "Miltônia 5". Both were formed by deep tropical weathering of the Ipixuna formation with a total of 400 million tons of estimated reserves with available alumina on the order of 47.7% and reactive silica of 4.0%. The geological profile of the Miltônia deposits reveals eight horizons, with lateral variation in thickness. The horizons are distinguished from the top to the bottom as follows: Clay overburden (CAP), nodular bauxite (BN), crystallized nodular bauxite (BNC), ferruginous laterite (LF), crystallized bauxite (BC), crystallized – amorphous bauxite (BCBA), amorphous bauxite (BA) and variegated clay (ARV) (Carvalho et al., 1997). The nodular bauxite is characterized by nodules that increase in size towards the base and form discontinuous bodies.

With increasing depth, the nodular bauxite transforms into crystallized nodular bauxite, constituted by nodules and concretions of reddish color. The combined thickness of BN and BNC is 2m on average. Table 3.1 presents the estimated quality of each layer for the Miltônia plateau (Silva et al., 2008). It can be seen that the ore variation at each depth is significantly high. The Paragominas plant was designed to operate with the BC bauxite, which is considered as "ore". The BC layer presents the higher Al_2O_3 to SiO_2 weight ratio (4.5-9.5) in the ore body. Recently, the BCBA bauxite layer, a marginal quality bauxite ore, has been processed combined with the BC layer but recoveries are lower than expected. The BNC and BN are also considered as "marginal ores" but exhibit higher clay concentrations than BC and BCBA.

For this research, a BNC bauxite sample of 30 kg provided by Vale Inc. was received in April, 2010 and 65 kg of BN bauxite was received in June, 2011 at the Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah.

3.2 Mineralogical Analysis

Analysis of the mineralogical composition can be made using the X-ray diffraction (XRD) technique, which reveals information about the crystallographic structure of the sample. Since the 1920s, XRD has been the principal method for identifying minerals in unknown substances through comparison with a data base of a standard or reference mineral (Scapin, 2003). Peaks were collected in the range of 5-65 degrees and the patterns were compared with the pattern library to identify the best-fitting peaks with the database. X-ray diffraction analyses were conducted to confirm the minerals present in the samples from the bauxite deposits of Paragominas and to confirm the data available in the literature.

Table 3.1. Characteristics from the Bauxite Ore by Layer from Miltônia Plateau at Paragominas, Brazil (Silva et al., 2008).

Bauxite layer	**Available Al_2O_3**	**Reactive SiO_2**	**Iron oxide Fe_2O_3**	**Depth (m)**	**Thickness average (m)**	**Classification**
BN	30-36%	5-10%	12-18%	17	1.0	Marginal Ore
BNC	34-42%	4-6%	8-17%	18-19.5	1.5	Marginal Ore
LF	22-29%	5-7%	15-45%	19.5-21	0.8	Waste
BC	36-47%	5-8%	8-38%	21-25	1.5	Ore
BCBA	46-48%	6-9%	7-9%	25-28	2.5	Marginal Ore
BA	45-47%	9-12%	6-7%	28-29	0.5	Waste

As indicated from previous studies, the presence of gibbsite, kaolinite, hematite and anatase were expected but the presence of quartz was questionable. The samples were prepared for the direct Rietveld analysis technique in a Rigaku Diffractometer and the patterns were analyzed by the program JADE.

The crushed samples as received were split and reduced to 500g. The subsample of 500g was pulverized using a vibratory pulverizer (ring mill). The vibratory pulverizer consists of two rings and a puck inside a grinding bowl (8" diameter). A 1HP motor is attached directly to a rotating eccentric to swing the bowl and components at a high speed (900 rpm) pulverizing the sample completely into less than 400 mesh. Usually, 3 to 5g are necessary for the mineralogical analysis so the pulverized material was split to 5g using a rotatory splitter. The surface of the packed particle bed prepared for XRD has to be flat and uniform for subsequent diffraction analysis.

3.3 Chemical Analysis

The elemental chemical composition of the Paragominas samples was determined using the X-ray fluorescence technique at the Technological Characterization Laboratory (LCT), Sao Paulo Polytechnic School, University of Sao Paulo, Brazil.

The analysis of major elements by X-ray fluorescence (XRF) is made possible by the behavior of atoms when they interact with X-rays. When materials are excited with high-energy, short wavelength radiation, such as X-rays, they become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the inner missing electron. This process releases energy due to the decreasing binding energy of the inner electron orbital compared to the outer electron. Since the energy of the emitted photon is characteristic of

a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the concentrations of elements that are present in the sample. The term fluorescence is applied to the phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy.

Sample preparation requires the dissolution of a portion of the sample by a fluxing salt during fusion to generate a homogeneous fused bead, eliminating the effect of particle size, orientation and mineralogy. The original samples were split to 500g after crushing and then divided into nine particle size fractions. The fusion procedure consists of heating a mixture of sample and flux at high temperatures, approximately 1100^{o}C, allowing the flux to melt and the sample to dissolve. The final product after cooling is a single-phase glass disc. Lithium tetraborate and lithium metaborate were used as fluxes. For a 1g sample to be analyzed, it is necessary to use 0.8g of lithium tetraborate and 0.2g of lithium metaborate. The XRF analyses were done with a PANalytical instrument, Axios Max – Minerals model.

3.4 Liberation Analysis

Automated systems for liberation analysis using energy-dispersive scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) are being used by mineral processing engineers because of their ability to generate data for characterization of mineral distributions, associations, and texture (Andersen et al., 2009). The QEMSCAN® is a widely used automated SEM-EDS technique. QEMSCAN stands for quantitative evaluation of minerals by scanning electron microscopy and is a registered trademark of the instrument marketed by the FEI Company. The QEMSCAN system identifies mineral phases in two dimensions using backscattered electron and secondary

electron signals, in combination with electron-induced secondary X-ray emission. Sample surface, grain size, mineral associations, mineral liberation and porosity can be characterized in 2D (Gottlieb et al., 2000).

Samples of bauxite ore from BN and BNC were prepared in polished sections for the feed, concentrate and tailing. The feed was divided into five size classes for liberation analyses as follows: 150-200 mesh, 200-270 mesh, 270-325 mesh, 325-400 mesh and <400 mesh and were evaluated for a preliminary estimation on the appropriate particle size for flotation feed. These samples were prepared and analyzed to determine the overall mineralogy, an estimate of liberation, and the association of alumina and silica minerals with iron oxide, before and after flotation. The concentrate and tailings were evaluated to check the separation efficiency. The method applied for analysis for the coarser size fractions was the particle mineral analysis (PMA) while for the finer size fractions, usually tailings, the samples were analyzed from field images.

The concentrate from reverse flotation experiments used for this analysis was divided into five size classes (100-150 mesh, 150-200 mesh, 200-270 mesh, 270-325 mesh and 325-400 mesh) for grade and recovery considerations. The tailings, mostly fine particles, were divided into particles + 400 mesh and – 400 mesh. The samples prepared for QEMSCAN consisted of polished-thin sections mounted on 25 mm-round epoxy plugs and were carbon-coated prior to analysis.

3.5 Desliming Experiments

The removal of the fines, less than 15 microns for the BNC bauxite ore and less than 38 microns for the BN bauxite ore, initially was made through sedimentation and decantation using a 1.0 liter cell with 40% solids. The pH was adjusted to pH 10.5, using

sodium hydroxide (2%), and then the slurry was agitated for 3 minutes and rested for 3 more minutes. The water with solids in suspension was removed using a tube until the 60% solids level line previously calibrated was reached. In the case of BN bauxite ore, the cell was filled with water again to achieve 1.0 liter volume level and this procedure was repeated twice removing particles less than 38 microns. The product from this operation is called deslimed and is used for the flotation experiments with desliming.

3.6 Direct Flotation Experiments

The recovery of the aluminum oxide minerals, in this case gibbsite, in the froth phase is called direct flotation. The flotation feed samples were crushed to minus 1.4mm and ground in a rod mill at 50% solids to produce a 90% minus 150 mesh flotation feed material. The flotation strategy consisted of one rougher stage for the analysis of the effect of reagents, and one or two cleaner stages for the optimum flotation conditions analysis as shown in Figure 3.1. The percent solids by weight during rougher flotation was 25% (approximately 300 g of bauxite in a 1 liter Denver cell considering 2.84 g/cm³ as the specific gravity of bauxite). Sodium carbonate was used as dispersant for kaolinite and for pH control. Sodium silicate was used for depression of the iron oxides and kaolinite while alkyl hydroxamate (mono-carboxylic fatty acid, 5-7% , and alkyl alcohol, 30-60%), named XD 903, produced by Cytec Industries Inc., was used as collector. The conditioning time was 3 minutes after pH adjustment and addition of reagents, the rougher stage was 5 minutes and the cleaner stages, 3 minutes. Sodium hydroxide (2%) was used for pH adjustment (pH 10.5 – pH 11.0). After flotation, the products were filtered and dried in the oven for 2 hours at 90^{o}C and the respective weights recorded for mass balance calculations.

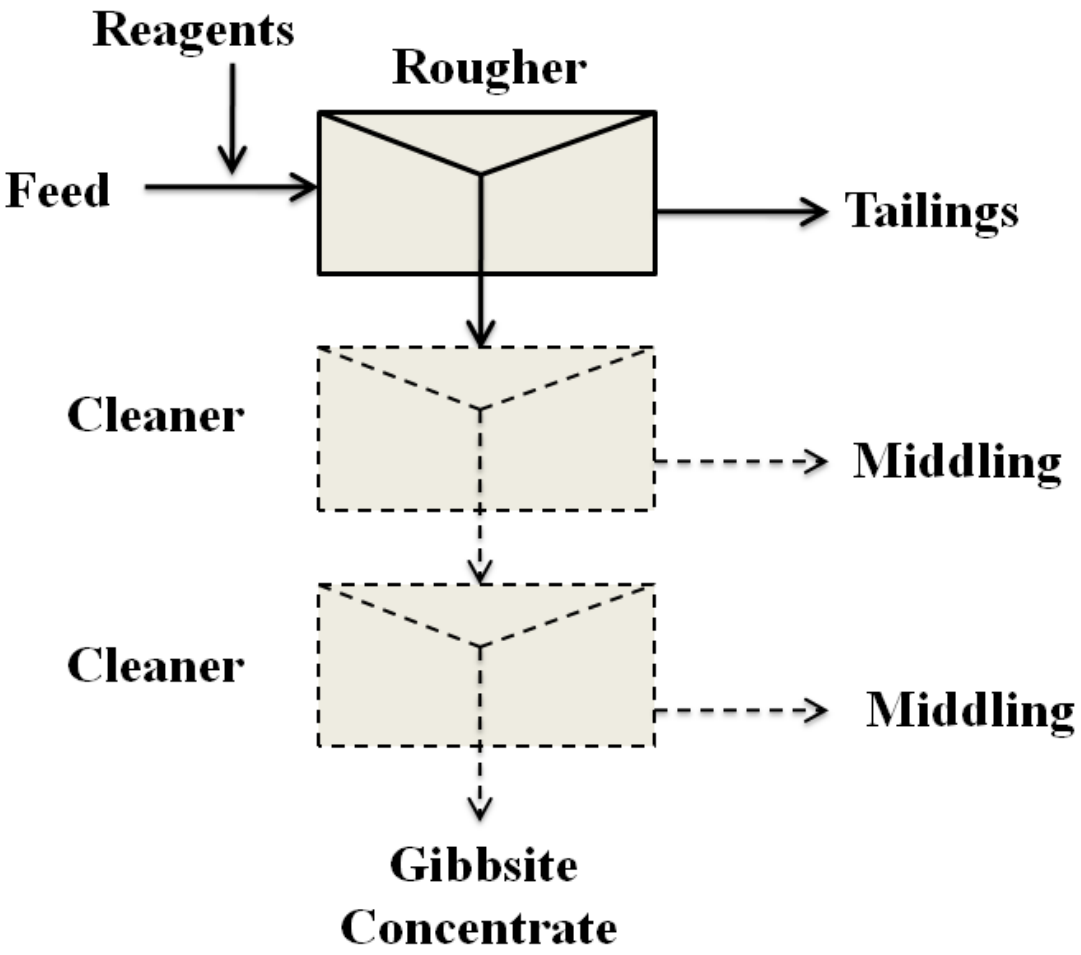

Figure 3.1. Direct flotation strategy considered for flotation with the froth phase being the gibbsite concentrate and the tailings and middlings as the depressed phase being the kaolinite tailings. Traced lines representing the possibilities used in some experiments.

3.7 Reverse Flotation Experiments

For the flotation of kaolinite, reverse flotation experiments, the feed sample was prepared using the same procedure as used for direct flotation. The flotation strategy consisted of one rougher stage, for the analysis of the effect of reagents addition, and one or two scavenger stages for the optimum flotation conditions experiments as shown in Figure 3.2. The conditioning time was 3 minutes, the rougher flotation, 5 minutes, and scavenger stages, 3 minutes.

The percent solids by weight during rougher flotation was 25% (approximately 300 grams of bauxite in a 1 liter Denver cell) and 2% sulfuric acid was used for pH adjustment. Sodium hexametaphosphate (+80 mesh, 96% from Aldrich Chemicals) was used in solution for the dispersion of fines while for depression of the iron oxide minerals, in this case hematite, a modified starch (HX-927 from Cytec Inc.) was used. For these reverse experiments, three condensate amine acetate (also called fatty amido-amine acetate) collectors supplied by Arr Maz Chemicals Inc. were evaluated, and one of them was selected for further flotation experiments. The flotation products were filtered and dried in the oven for 2 hours at 90^{o}C and then the respective weights recorded for mass balance calculations.

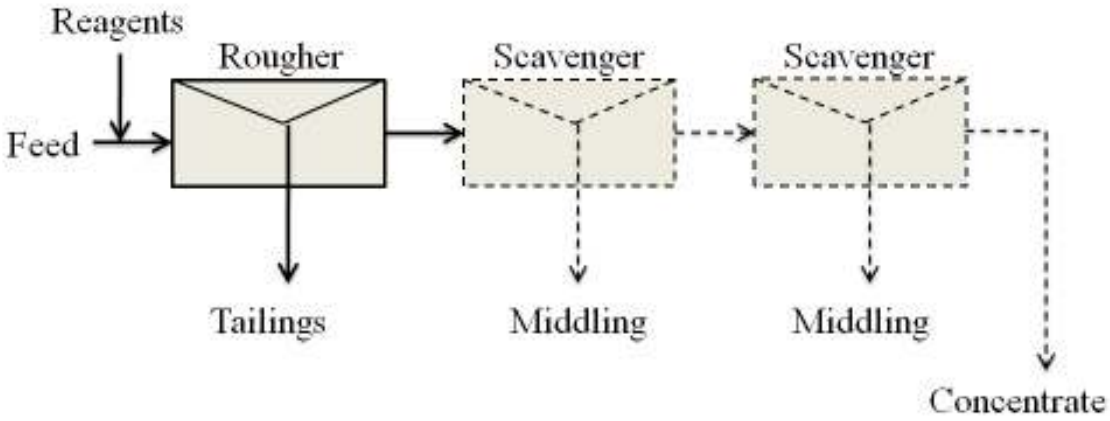

Figure 3.2. Reverse flotation strategy considered for the flotation of kaolinite where the tailings and middlings represent the froth phase. Traced lines represent the different strategies considered.

CHAPTER 4

RESULTS

4.1 Sample Characteristics

4.1.1 X-Ray Diffraction

The bauxite samples obtained from the Paragominas bauxite complex are composed basically of aluminum minerals, alumino-silicates and oxides. Table 4.1 presents the estimated mineralogical analysis of the BN and BNC bauxite samples based on XRD spectra shown in Figures 4.1 and 4.2. For bauxite ore types, a significant presence of gibbsite is observed followed by kaolinite, the main clay mineral, hematite as the primary iron mineral and anatase as the titanium mineral.

Based on the geological profile of the Miltônia plateau, the presence of quartz was uncertain due to the position of the quartz layer at the very bottom of the ore body. Since the BN and BNC layers are not deep into the ore body, significant quartz is not expected to be found in either sample. From the XRD results, this assumption was confirmed and no evidence of the presence of quartz was found at a concentration higher than 2%, which is the level range detected by XRD. For this reason, it is assumed that the presence of quartz is insignificant from a flotation perspective. Another important aspect for discussion is the mineral distribution in the very fine particle size fraction. XRD analysis reveals that gibbsite is present in the -400 mesh size fraction but at a lower concentration than in the coarse particle size fraction. This assumption was confirmed by chemical and

Table 4.1. Estimated mineral distribution for the BN and BNC bauxite ore samples in % by mass from XRD and chemical analysis.

	Gibbsite	**Kaolinite**	**Hematite**	**Anatase**	**Quartz ***
BN	64-67	12-14	4.0-8.0	1.0-3.0	1.0-2.0
BNC	67-70	10-12	2.0-6.0	1.0-3.0	1.0-2.0

* Estimated based on optical microscopy images.

liberation analyses where the presence of gibbsite was analyzed in terms of liberated particles or locked particles disseminated in other host minerals. Analysis from optical microscopy identified the presence of a few grains of quartz for both bauxite ores and was estimated to be from 1.0% to 2.0%.

The presence of gibbsite in the small particle size fractions is attributed to the natural breakage of coarser particles during the handling of the sample and the removal of the particles less than 400 mesh will significantly affect the overall gibbsite recovery. Even after a mechanical breakage, such as crushing and grinding, it is natural that some liberated gibbsite particles report to the very fine particle size classes together with a higher concentration of kaolinite.

4.1.2 Scrubbing Process

Prior to receiving the samples in Utah, both BN and BNC bauxite ores were treated by conventional laboratory scrubbers, which consist of a vibratory screen with

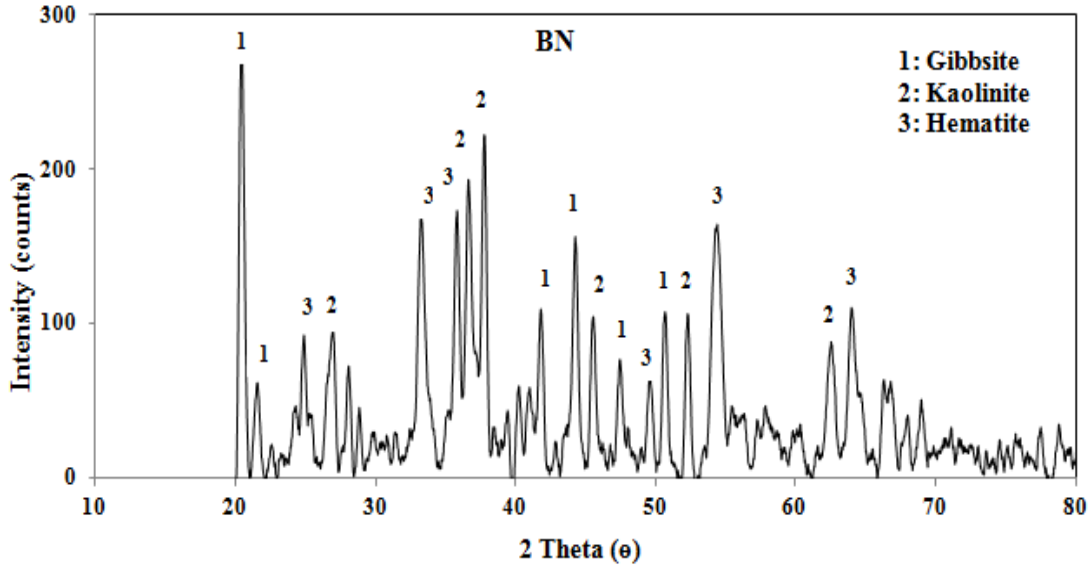

Figure 4.1 X-ray diffraction patterns of the BN bauxite ore from Paragominas deposit, Brazil.

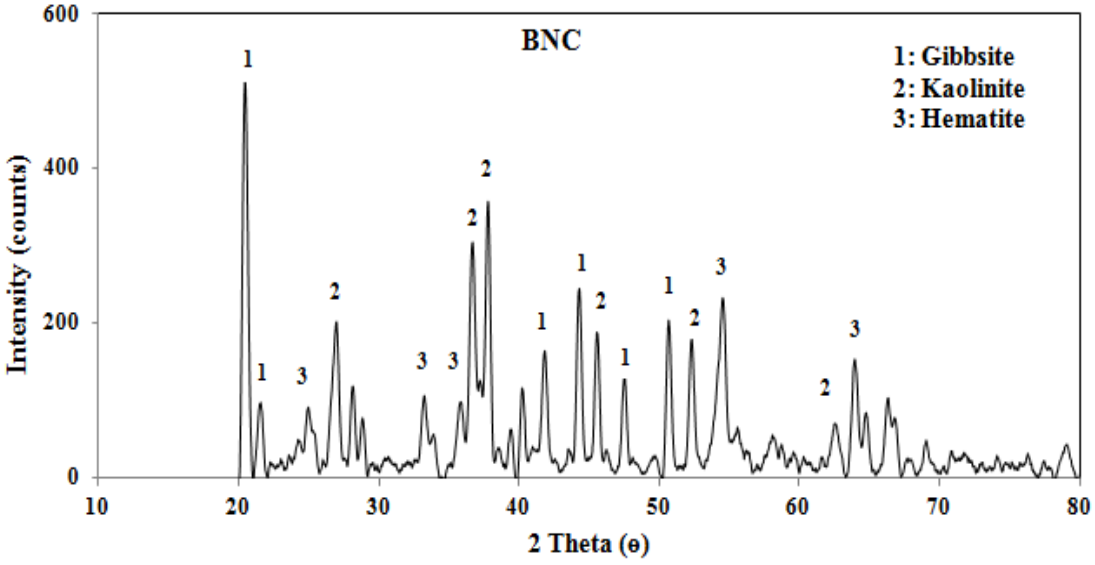

Figure 4.2 X-ray diffraction patterns of the BNC bauxite ore from Paragominas deposit, Brazil.

water added at the top to remove particles less than 400 mesh, considered as natural fines only.

No size reduction was performed until washing in the scrubbers. The minus 400 mesh material contains a high concentration of kaolinite. The objective of this treatment is to increase the Al_2O_3 to SiO_2 ratio prior to sample preparation for flotation experiments and also to correspond with the current industrial process. The chemical analysis prior to scrubbing done at the Paragominas plant laboratory in Brazil is shown in Table 4.2 for the BN bauxite ore and in Table 4.3 for the BNC bauxite ore. In the case of BN bauxite ore, particles less than 400 mesh represents 20.2% of the total weight and after removal the SiO_2 in the plus 400 mesh materials is reduced from 11.6% to 9.92% with an Al_2O_3 recovery of 82.1%. The bauxite ores received in Utah were products from the scrubbing process. On the other hand, the high grade marginal bauxite ore, BNC, exhibited 24.4% of particles less 400 mesh by weight and by removing the minus 400 mesh material, the SiO_2 dropped from 9.71% to 7.73% with an Al_2O_3 recovery of 77.6%.

4.1.3 Chemical Analysis

The chemical composition determined by XRF for the samples of BN and BNC bauxite ores after scrubbing and as received at the University of Utah are show in Tables 4.4 and 4.5. The samples received for analysis were separated into nine size fractions for chemical analysis. As expected, the BNC exhibited a slightly higher amount of aluminum oxide and a lower concentration of silica oxide, being considered as a medium quality bauxite ore or high grade marginal ore. The finer particle size classes also exhibit a higher concentration of silica and less alumina for both bauxite ores.

Table 4.2 Chemical analyses (XRF) of the BN bauxite ore by size fractions, in % by mass prior to scrubbing.

Size, mesh	Fraction weight	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Al_2O_3/ SiO_2
+ 20	0.258	49.6	6.72	16.4	1.21	7.38
20 x 48	0.142	48.2	7.84	17.9	1.22	6.15
48 x 65	0.088	47.2	9.21	18.2	1.32	5.12
65 x 100	0.078	45.5	10.7	18.3	1.91	4.25
100 x 150	0.077	42.0	12.2	19.9	4.96	3.44
150 x 200	0.062	39.1	14.4	20.2	6.43	2.71
200 x 270	0.053	39.3	16.2	19.3	4.22	2.43
270 x 400	0.042	40.1	18.3	21.1	1.71	2.19
- 400	0.202	39.7	18.1	21.0	1.71	2.19
Total	1.00	44.7	11.6	18.7	2.1	3.85
Total without – # 400		45.9	9.92	18.11	2.26	4.62

Loss on ignition: 22.7% (1g of sample dried at 1050^{o} C for 1 hour).

Table 4.3 Chemical analyses (XRF) of the BNC bauxite ore by size fractions, in % by mass prior to scrubbing.

Size, mesh	Fraction weight	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Al_2O_3/ SiO_2
+ 20	0.265	54.6	5.20	7.44	1.28	10.5
20 x 48	0.153	54.6	5.52	7.91	1.29	9.89
48 x 65	0.078	54.3	6.92	8.54	1.33	7.85
65 x 100	0.059	52.1	8.57	9.27	1.87	6.08
100 x 150	0.059	48.1	10.3	10.8	4.26	4.67
150 x 200	0.062	44.7	12.6	11.5	5.28	3.55
200 x 270	0.048	44.8	14.6	11.6	4.05	3.07
270 x 400	0.032	45.9	15.9	12.2	1.94	2.89
- 400	0.244	46.3	15.8	12.2	1.77	2.93
Total	1.00	50.7	9.71	9.67	2.02	5.22
Total without – # 400		52.1	7.73	8.85	2.09	6.74

Loss on ignition: 26.4% (1g of sample dried at 1050^{o} C for 1 hour).

Table 4.4 Chemical analyses (XRF) of the BN bauxite ore by size fractions, in % by mass as received in Utah.

Size, mesh	Fraction weight	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Al_2O_3/ SiO_2
+ 9	0.379	49.5	7.48	16.7	1.26	6.62
9 x 14	0.189	49.2	7.43	17.4	1.26	6.62
14 x 20	0.147	48.8	7.80	17.8	1.24	6.25
20 x 30	0.058	48.7	8.33	18.0	1.25	5.85
30 x 35	0.018	48.3	8.57	18.3	1.26	5.64
35 x 40	0.023	48.1	8.97	18.5	1.27	5.36
40 x 50	0.032	47.6	9.4	18.5	1.26	5.06
50 x 60	0.008	46.5	10.6	19.0	1.30	4.39
- 60	0.137	41.2	15.0	20.8	2.48	2.75
Total	1.00	47.7	8.69	17.7	1.42	5.49

Loss on ignition: 24.1% (1g of sample dried at 1050^o C for 1 hour).

Table 4.5 Chemical analyses (XRF) of the BNC bauxite ore by size fractions, in % by mass received in Utah.

Size, mesh	Fraction weight	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Al_2O_3/ SiO_2
+ 9	0.095	55.7	7.86	5.97	1.46	7.09
9 x 14	0.189	54.8	8.79	5.96	1.65	6.23
14 x 20	0.205	55.5	6.39	7.32	2.27	8.68
20 x 30	0.242	53.6	8.43	7.61	2.01	6.36
30 x 35	0.116	54.9	7.46	8.03	1.82	7.36
35 x 40	0.101	54.6	7.61	7.91	1.58	7.17
40 x 50	0.026	54.2	7.72	8.02	1.53	7.02
50 x 60	0.023	53.4	9.07	8.15	1.53	5.89
- 60	0.002	51.1	12.2	7.57	1.82	4.19
Total	1.00	54.7	7.83	7.18	1.85	6.99

Loss on ignition: 28.5% (1g of sample dried at 1050^{o} C for 1 hour).

The BN bauxite ore, considered as a low grade marginal bauxite ore, exhibited an Al_2O_3 to SiO_2 ratio of 5.49 while the BNC bauxite ore exhibited an Al_2O_3 to SiO_2 ratio of 6.98. It is believed that the BNC sample taken from the Miltônia 3 plateau was obtained from a region close to the boundary layer between BN and BNC since the BNC quality shows a slightly lower grade compared to the data reported in the literature.

The flotation feed particle size after crushing and rod-mill grinding is shown in Table 4.6 and a significant amount of material is found in the -400 mesh size class, 41%. The rod-mill grinding was chosen over the ball mill to avoid further generation of fine particles during the size reduction operation.

4.2 Direct Flotation

Direct flotation experiments for BN and BNC bauxite ores were carried out in a Denver 1L cell with 25% solids. During the evaluation of depressants, dispersants and pH, one rougher stage was used with different levels of the desired variable, keeping all others variables constant throughout the experiments. For the evaluation of collector dosage, one rougher and one cleaner stage was used to determine the preferred flotation conditions. Direct flotation with and without desliming was performed after rod-mill grinding at 50% solids, with approximately 80% of the product passing in 106 microns. The experiments were performed in a 1L Denver cell at 1300 rpm. After pH adjustment and reagent addition, the conditioning time was 3 minutes. The rougher flotation stage was performed in 4 minutes and cleaner in 3 minutes. The effects of dispersants, depressants and collector dosages were evaluated during the direct flotation of gibbsite where the froth phase represents the gibbsite concentrate.

Table 4.6 Particle size distribution after 12 minutes rod-mill grinding at 50% solids from a feed 100% passing 14 mesh used as flotation feed.

	% Retained	**% Passing**
140 Mesh	23.8	76.2
200 Mesh	14.0	62.1
270 Mesh	15.0	47.1
325 Mesh	2.92	44.2
400 Mesh	3.03	41.2
< 400 Mesh	41.2	
P80 (microns)	113	

4.2.1 Effect of Alkyl Hydroxamate on Direct Flotation

The effect of collector dosage addition on the direct flotation of gibbsite is shown in Figures 4.3 to 4.6 with respect to Al_2O_3 grade in the concentrate and SiO_2 recovery in the tailings using alkyl hydroxamate, XD 903, at pH 10.5 with 6.0 kg / ton and 6.5 kg / ton of sodium carbonate for the BN and BNC bauxite ores respectively and 1.5 kg / ton of sodium silicate. The maximum Al_2O_3 recovery for the BN cleaner concentrate was found to be 62.8% at a collector concentration of 3.0 kg / ton and 78.4% in the BNC concentrate using 2.5 kg / ton of hydroxamate. With respect to the cleaner concentrate quality, the highest Al_2O_3 grade of 49.4% with 9.68% SiO_2 at 1.5 kg / ton was obtained in the BN bauxite ore while for the BNC, 58.2% Al_2O_3 and 5.9% SiO_2 in the concentrate with 2.0 kg / ton was achieved after one cleaner flotation stage.

It is evident that at low collector dosage, grades are higher and with increasing collector dosage, the recoveries increase both for direct and reverse flotation with a decrease in selectivity. Another important correlation is the mass recovery and collector addition. As the collector addition increases, the yield (for both reverse and direct flotation) increases. Comparing the direct flotation results to reverse flotation, the collector addition is significantly higher (2.5kg / ton for the direct flotation against 0.4 kg / ton for the reverse flotation). The mineral concentration may explain the reagent dosage schedule since the gibbsite mass represents 70-75% by mass and the kaolinite, 10-15% by mass.

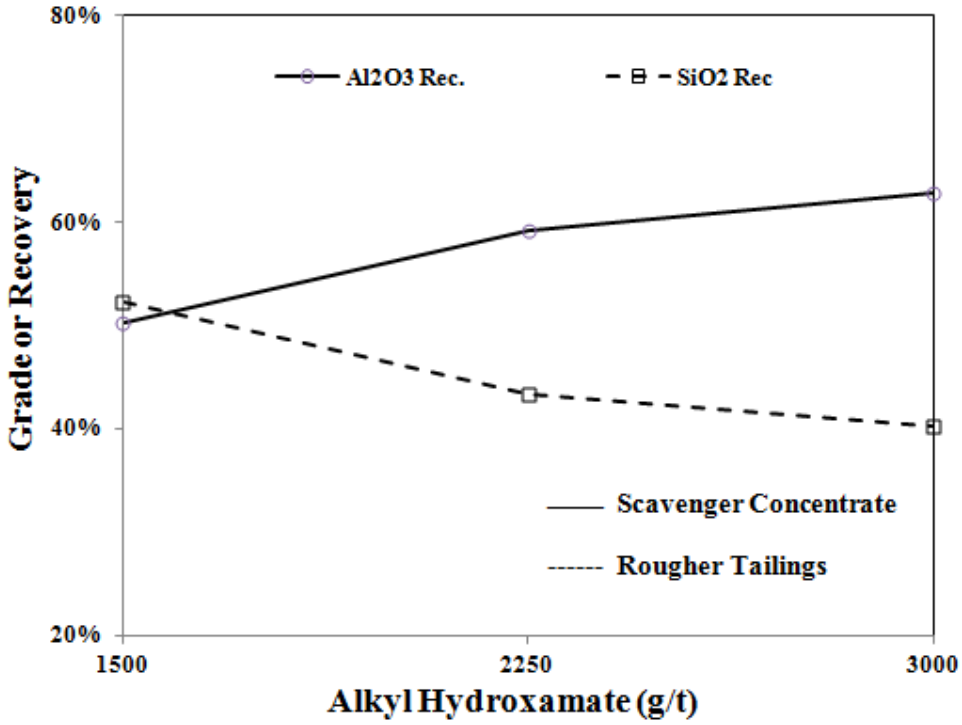

Figure 4.3 Effect of alkyl hydroxamate on recovery for direct flotation without desliming for the BN bauxite ore, 80% passing 113 microns, pH 10.5.

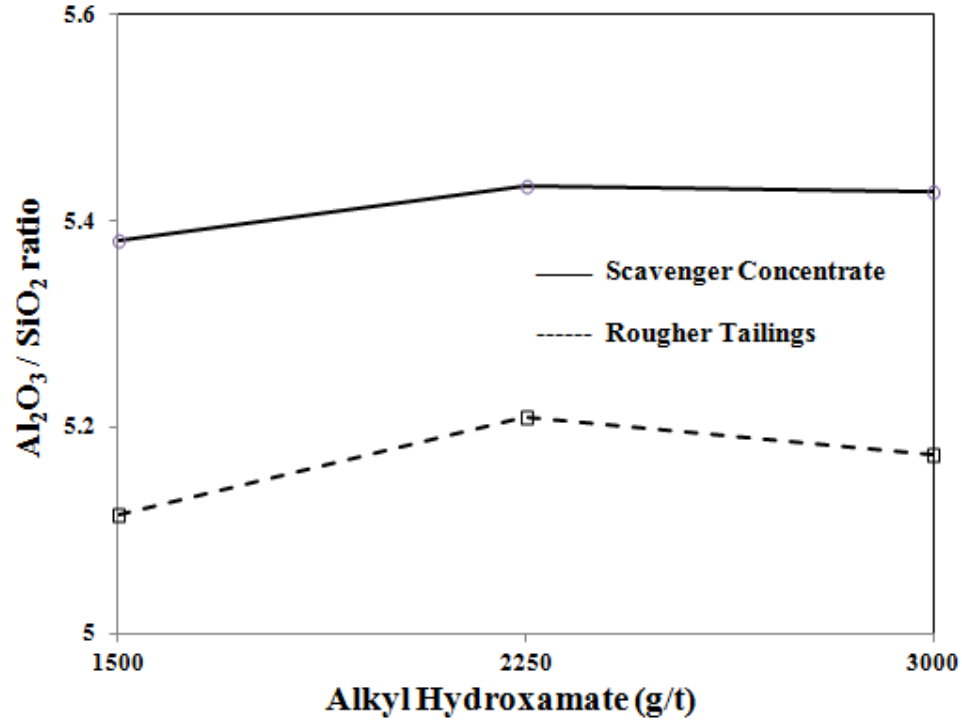

Figure 4.4 Effect of alkyl hydroxamate on grade for direct flotation without desliming for the BN bauxite ore, 80% passing 113 microns, pH 10.5.

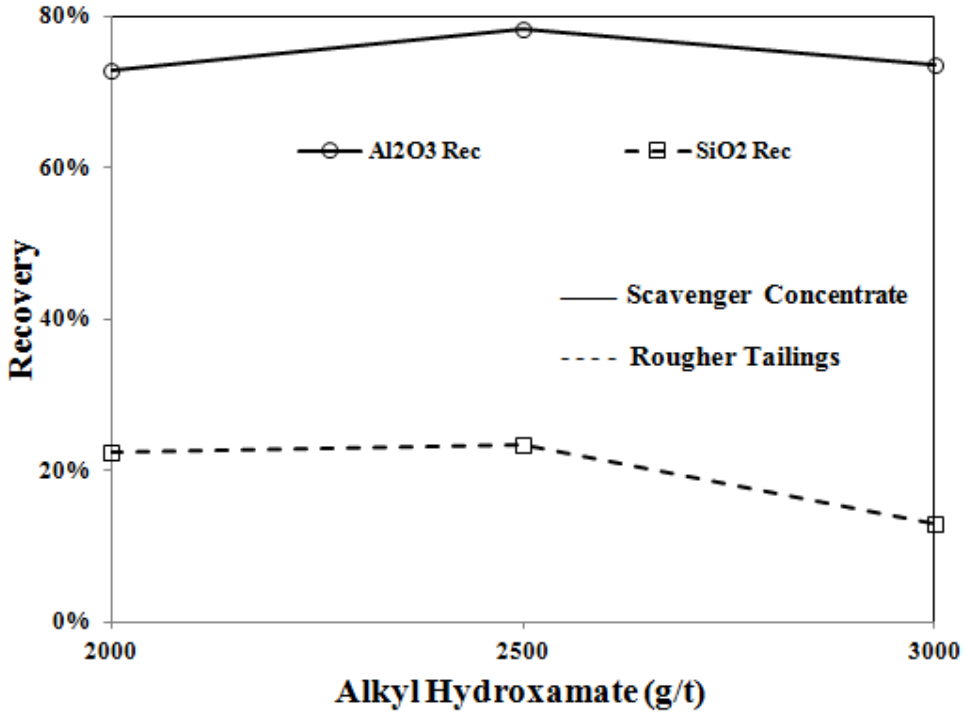

Figure 4.5 Effect of alkyl hydroxamate on recovery for direct flotation without desliming with BNC bauxite ore, 80% passing 113 microns, pH 10.5.

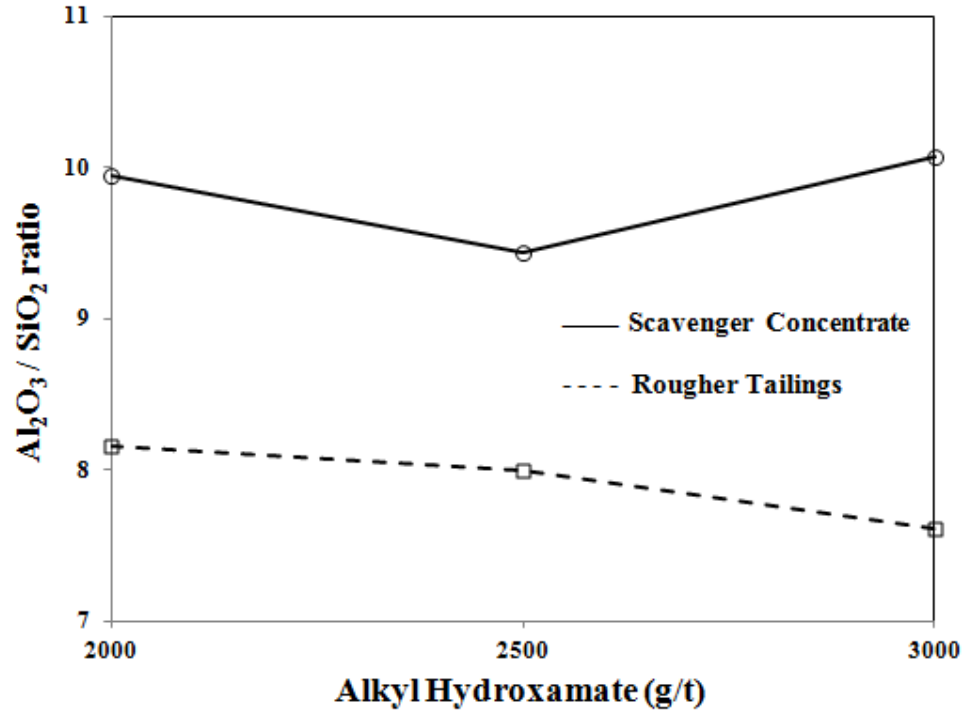

Figure 4.6 Effect of alkyl hydroxamate on grade for direct flotation without desliming with BNC bauxite ore, 80% passing 113 microns, pH 10.5.

4.2.2 Effect of Sodium Carbonate on Direct Flotation

The effect of sodium carbonate as a kaolinite dispersant was evaluated during the direct flotation of gibbsite without desliming using 2.25 kg / ton of alkyl hydroxamate, at pH 10.5 for one rougher flotation stage at 25% solids and is shown in Figures 4.7 and 4.8. In terms of Al_2O_3 recovery, the concentrations of 4.0 and 8.0 kg / ton exhibited a maximum of 62.9% while in terms of Al_2O_3 grade, the concentration of 8.0 kg / ton presented a slightly higher grade of 49.2% Al_2O_3 over the two concentrations. The optimum rougher concentrate quality was achieved using 2.0 kg / ton where an Al_2O_3 to SiO_2 ratio of 5.62 was obtained. In summary, at high dosages, the fine particles of kaolinite will be more dispersed and less attached to gibbsite particles resulting in higher Al_2O_3 recoveries. For more efficiency in terms of grade, the high concentration of sodium carbonate has to be combined with sodium silicate, which will maximize the separation efficiency throughout flotation.

4.2.3 Effect of Sodium Silicate on Direct Flotation

The addition of sodium silicate as depressant for the iron oxide minerals such as hematite was evaluated during the direct flotation of gibbsite using 2.25 kg / ton of alkyl hydroxamate, 6.0 kg / ton of sodium carbonate, at pH 10.5 for one rougher flotation at 25% solids and is shown in Figures 4.9 and 4.10. At a concentration of 2.0 kg / ton of sodium silicate, the Al_2O_3 recovery in the concentrate reached its maximum of 63.6% but the SiO_2 recovery in the concentrate was also high, 60.4%. The optimum Al_2O_3 to SiO_2 ratio was found to be in the range of 1.0 to 1.5 kg / ton of sodium silicate addition among all dosages.

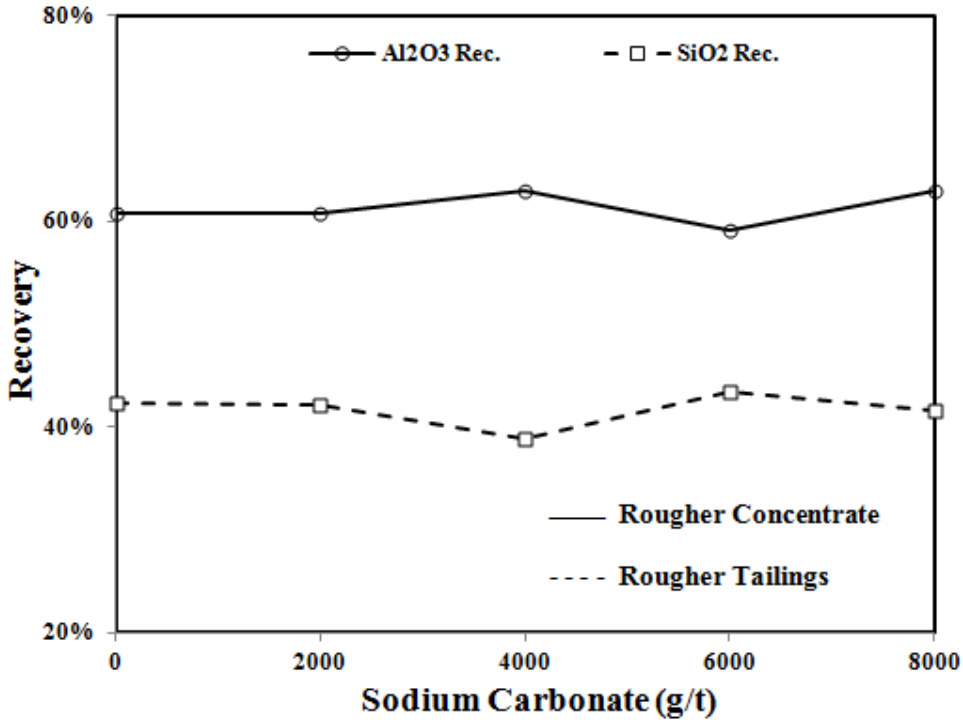

Figure 4.7 Effect of sodium carbonate on recovery for direct flotation without desliming for BN bauxite ore, 80% passing 113 microns, pH 10.5.

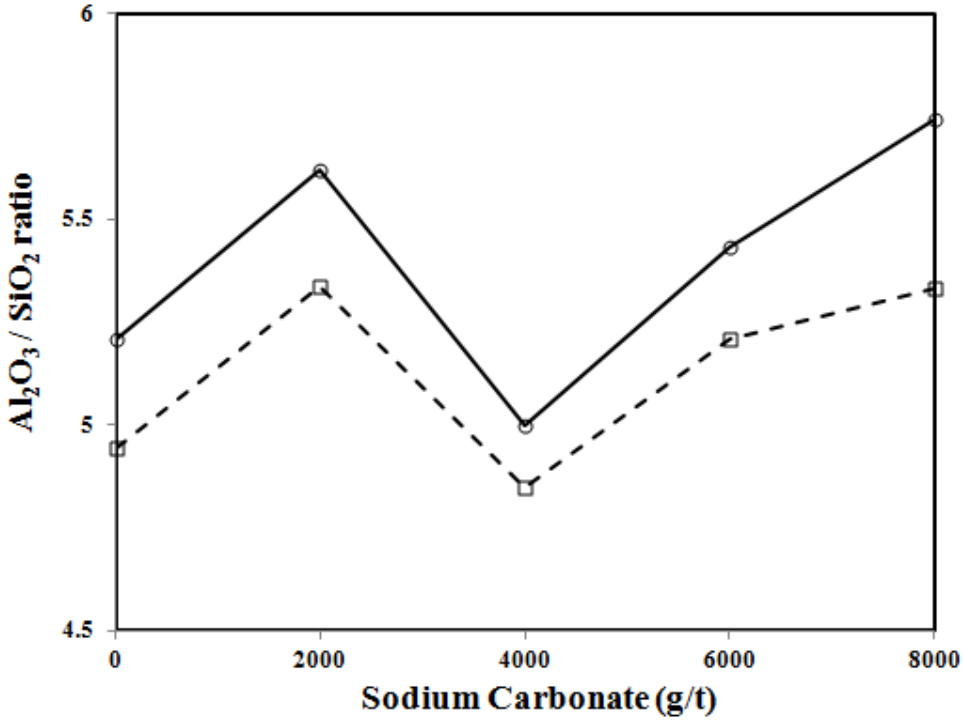

Figure 4.8 Effect of sodium carbonate on grade for direct flotation without desliming for BN bauxite ore, 80% passing 113 microns, pH 10.5.

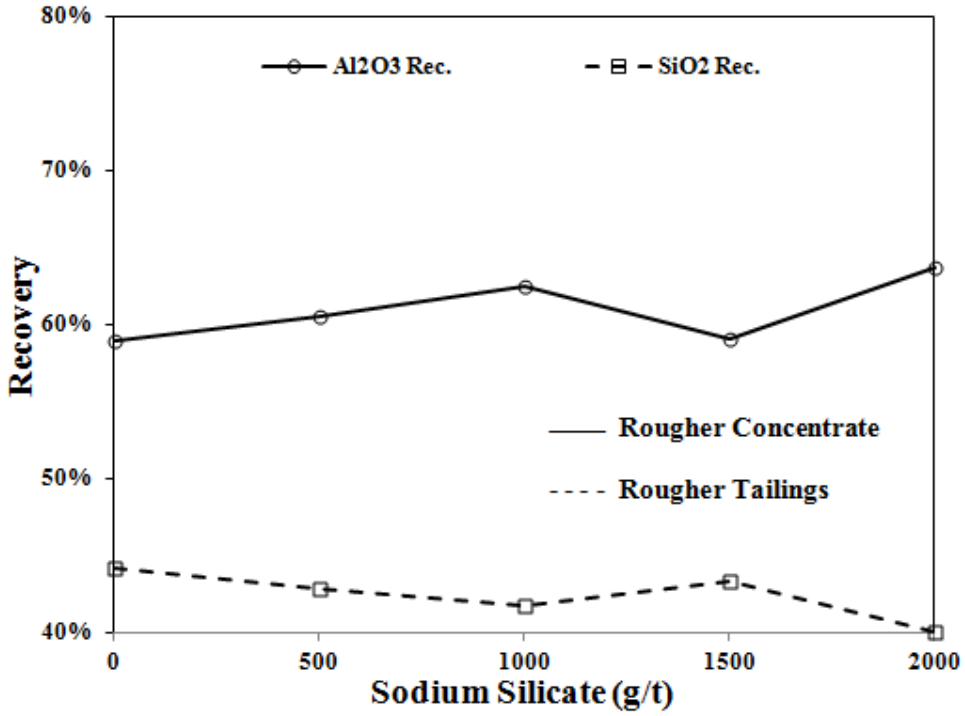

Figure 4.9 Effect of sodium silicate on recovery for direct flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 10.5.

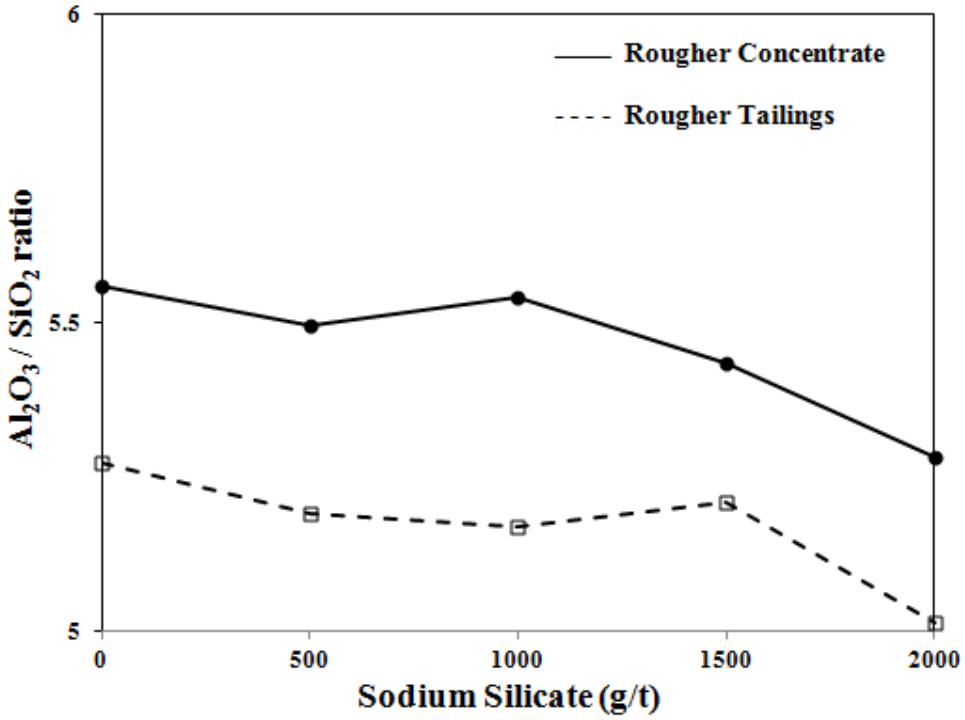

Figure 4.10 Effect of sodium silicate on grade for direct flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 10.5.

From the results above, a concentration dosage of 1.5 and 2.0 kg / ton can be chosen based upon either a grade or recovery perspective. At a higher depressant dosage, the gibbsite recovery in the concentrate will be higher.

4.2.4 Effect of Alkyl Hydroxamate on Direct Flotation with Desliming

The effect of alkyl hydroxamate concentration on the direct flotation of gibbsite with desliming is shown in Figures 4.11 to 4.14 for BN and BNC bauxite ores using 0.5 kg / ton and 0.4 kg / ton of sodium carbonate and 0.15 kg / ton and 0.1 kg / ton of sodium silicate respectively. As the collector dosage increases, the Al_2O_3 recovery also increases reaching its maximum at 52.2% (1.85 kg / ton) and 74.3% (2.5 kg / ton) for the BN and BNC respectively. With respect to concentrate grade, the BN bauxite ore exhibited a ratio of 8.44 which was found at a 1.25 kg / ton dosage of hydroxamate while for the BNC bauxite ore an Al_2O_3 to SiO_2 ratio of 10.6 at a 1.0 kg / ton dosage was found.

The effect of desliming on flotation response has been significant in the flotation behavior for both direct and reverse flotation with different bauxite ore types. For example, during the reverse flotation of kaolinite without desliming, the optimum collector dosages for the BN and BNC bauxite ores with respect to recovery were 400 and 300 g / ton reaching 57.3% and 80.8% Al_2O_3 recovery. After desliming recovery rose to 73.5% and 84.3% using 200 and 100 g / ton, respectively. Despite the particular behavior of the collector reduction and higher recoveries, the effect of desliming prior to flotation produces different results with respect to product quality among the bauxite ore types. In the case of the BN flotation, when the collector dosage was increased from 300 to 400 g / ton the result was a lower quality concentrate with an Al_2O_3 to SiO_2 ratio of 6.07 (400 g / ton) in contrast to a ratio of 7.41 (300 g / ton) without desliming.

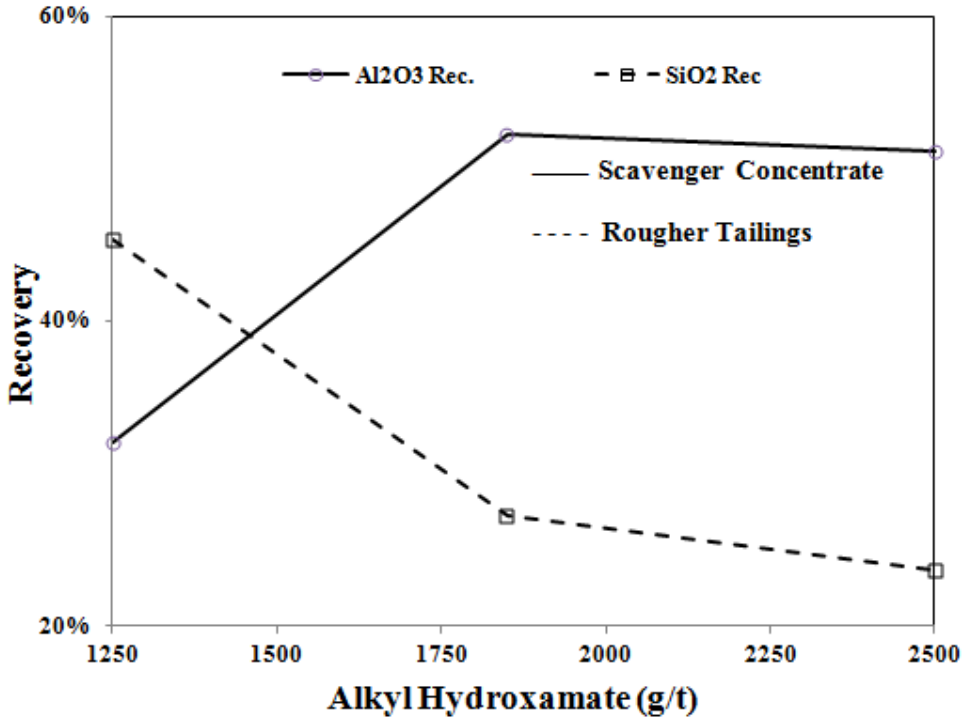

Figure 4.11 Effect of desliming on recovery for direct flotation with BN bauxite ore, 80% passing 113 microns, pH 10.5.

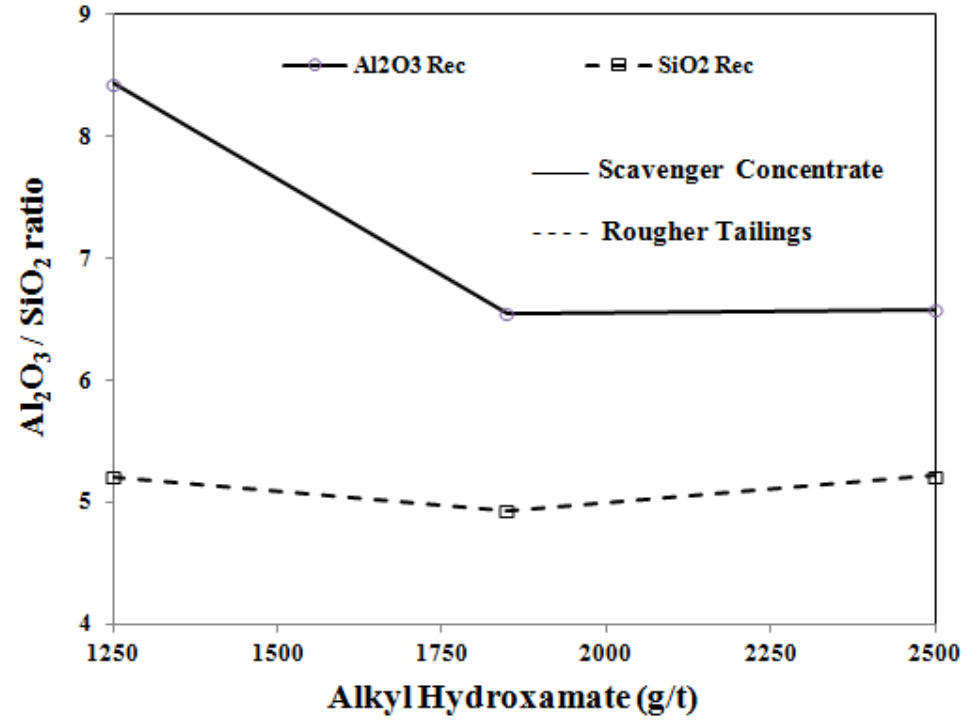

Figure 4.12 Effect of desliming on grade for direct flotation with BN bauxite ore, 80% passing 113 microns, pH 10.5.

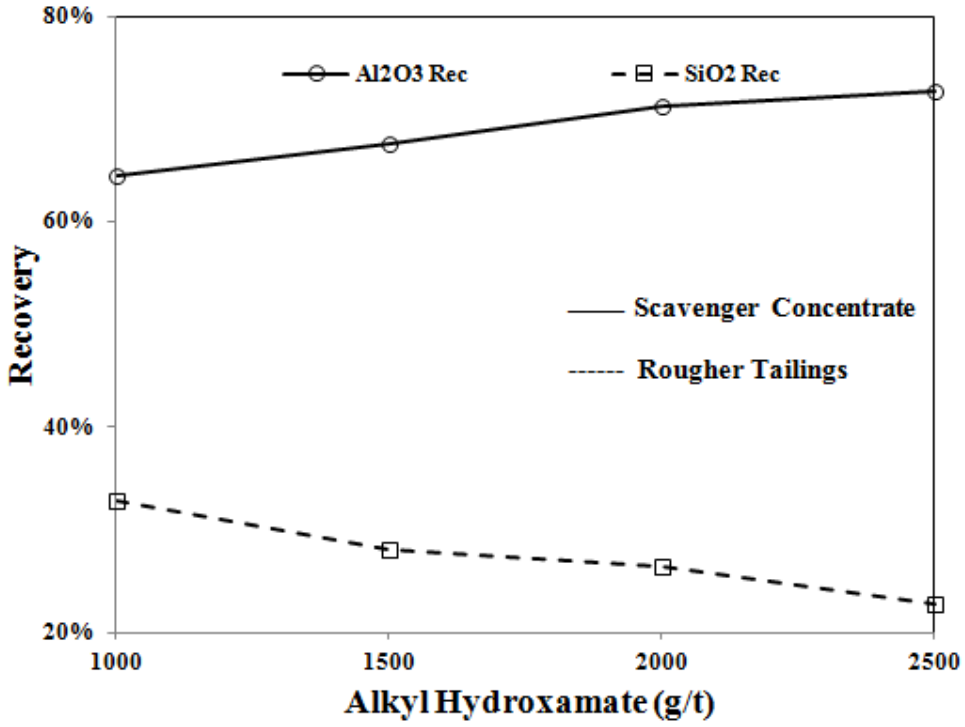

Figure 4.13 Effect of desliming on recovery for direct flotation with BNC bauxite ore, 80% passing 113 microns, pH 10.5.

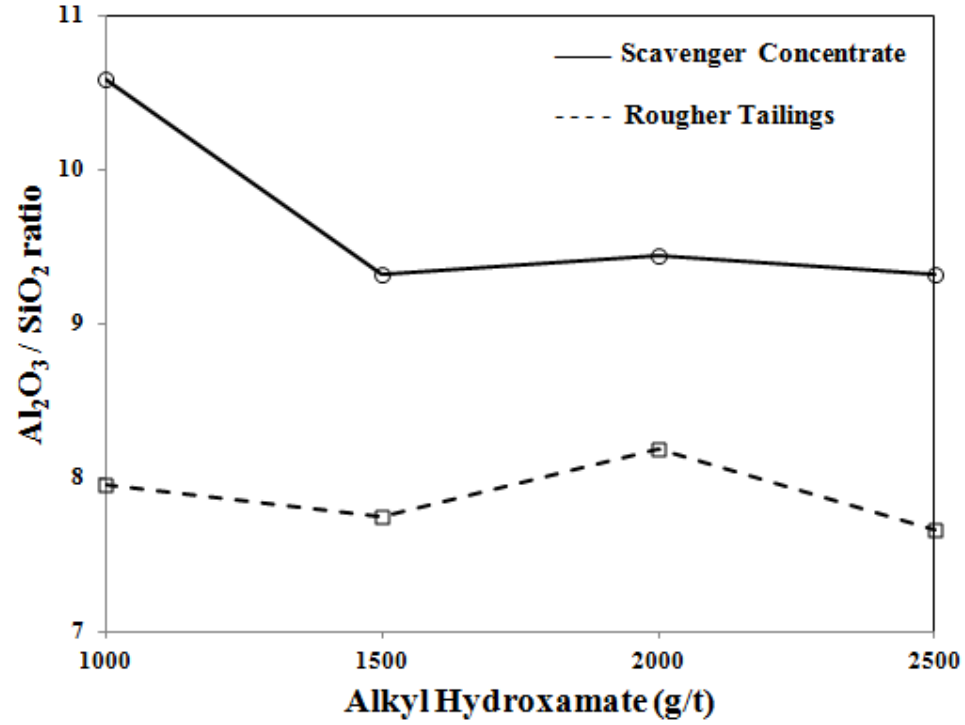

Figure 4.14 Effect of desliming on grade for direct flotation with BNC bauxite ore, 80% passing 113 microns, pH 10.5.

On the other hand, for the BNC flotation, the concentrate quality increased, with an Al_2O_3 to SiO_2 ratio of 12.1 compared to a 9.83 ratio, the collector dosage remaining the same (400 g / ton).

In the case of the direct flotation of gibbsite, the impact of desliming in flotation performance was also important but opposite from reverse flotation. For both BN and BNC, the recoveries were higher, but the grade dropped with an increase in collector dosage. As expected, recoveries are higher with flotation without desliming but grades are lower. On the other hand, flotation with desliming results in higher grades but lower recoveries. The effect of desliming has a significant impact on the SiO_2 recovery in the tailings. For example, the SiO_2 recovery during flotation with desliming was 27.2% at 1.85 kg / ton and 43.3% during flotation without desliming at a collector dosage of 2.25 kg / ton. In the case of SiO_2 grade, desliming did not impact the tailings quality. Regarding the Al_2O_3 recovery and grade, the effect of desliming was the opposite. While Al_2O_3 recovery was similar for both flotations with and without desliming, grades were higher when flotation with desliming was performed. The collector dosages were also impacted with desliming. At lower concentrations (1.25 kg / ton) the concentrate Al_2O_3 reached its maximum of 54.3% for the BNC bauxite ore compared to the 49.4% Al_2O_3 grade using 1.5 kg / ton collector dosage during flotation without desliming.

In summary, while desliming was beneficial for the reverse flotation for both recovery and collector dosages, it was not significant from the product quality perspective during direct flotation. On the other hand, during direct flotation, the desliming prior to flotation was detrimental for the recoveries but reduced significantly the collector dosage if a higher quality concentrate was to be produced.

4.2.5 Summary for Direct Flotation

Tables 4.7 to 4.8 show the flotation performance from direct flotation of gibbsite for the BN and BNC bauxite ores. The direct flotation of gibbsite without desliming, both for BN and BNC bauxite ores, exhibited higher Al_2O_3 to SiO_2 ratios (8.44 and 10.58). Direct flotation of gibbsite was also performed, but with better results using a deslimed feed at pH 10.5 in the rougher and cleaner flotation stages. The collector dosage range was 1.0 – 1.25 kg / ton, depressant 1.0 – 1.5 kg / ton and dispersant 4.0 – 5.0 kg / ton.

4.3 Reverse Flotation

Reverse flotation experiments for BN and BNC bauxite ores were carried out in a Denver 1L cell with 25% solids. During the evaluation of depressants, dispersants and pH, one rougher stage was used with different levels of the desired variable keeping all other variables constant throughout the experiments. For the evaluation of collector dosage, one rougher and one scavenger stage were used to determine the preferred flotation conditions.

Reverse flotation with and without desliming was performed after rod-mill grinding at 50% solids, with 80% of the product minus 106 microns. The experiments were performed in a 1L Denver cell at 1300 rpm. After pH adjustment and reagent addition, the conditioning time was 3 minutes. Rougher flotation stage was performed in 4 minutes and scavenger or cleaner stage in 3 minutes. The effect of dispersants, depressants, pH and collector dosages were evaluated during the reverse flotation of kaolinite where the froth phase represents the kaolinite tailings.

Table 4.7 Direct flotation of gibbsite of BN bauxite ore with desliming at 38 microns at pH 10.5 with 1.25 kg / ton alkyl hydroxamate, 1.0 kg / ton sodium silicate and 5.0 kg / ton sodium carbonate after one rougher and two cleaner flotation stages.

	Yield %	Grade		Recovery		Al_2O_3/SiO_2
		Al_2O_3	SiO_2	Al_2O_3	SiO_2	
Al_2O_3 Concentrate	28.4	53.4	6.3	32.0	18.4	8.44
Middlings	8.7	43.9	12.0	8.0	10.7	6.69
SiO_2 Tailings	41.7	45.1	10.6	39.7	45.3	5.21
Slimes	21.1	45.4	11.8	20.2	25.6	3.87
Feed	100	47.4	9.8	100	100	4.86

Table 4.8 Direct flotation of gibbsite of BNC bauxite ore with desliming at 15 microns at pH 10.5 with 1.0 kg / ton alkyl hydroxamate, 1.5 kg / ton sodium silicate and 4.0 kg / ton sodium carbonate after one rougher and one cleaner flotation stage.

	Yield %	Grade		Recovery		Al_2O_3/SiO_2
		Al_2O_3	SiO_2	Al_2O_3	SiO_2	
Al_2O_3 Concentrate	61.2	58.3	5.5	64.5	48.4	10.58
Middlings	10.5	52.8	9.8	10.1	14.8	9.37
SiO_2 Tailings	26.0	49.9	8.8	23.4	32.8	8.11
Slimes	2.3	51.1	12.2	2.1	4.0	7.95
Feed	100	55.4	7.0	100	100	7.95

4.3.1 Collector Selection for Reverse Flotation

Flotation without desliming was performed initially to select the appropriate collector for reverse flotation. Three customized amine reagents, custamines, produced by ArrMaz Custom Chemicals Inc., named UU 13, UU 17 and UU 18 were selected and tested. The customized UU 13 is a condensate amine acetate, also called fatty amido-amine acetate, where the condensate amine has been reacted with polyethylene amines and mixed with fatty acids at a mole ratio of 1.20 to 1.35 of fatty acids to amines. Reagents named UU 17 and UU 18 are also condensate amines with a fatty acid to amine ratio of 1.60 to 1.75 and with a different frother ratio.

The flotation configuration for these experiments was one rougher stage followed by one scavenger stage at pH 4.0 using 0.5 kg /ton of starch and 1.5 kg /ton of sodium hexametaphosphate (SHMP). Results are shown in Figures 4.15 to 4.18, and reveal the flotation responses among the reagents with respect to the concentrate recovery and grade. The Al_2O_3 recoveries in the concentrate using UU 13 and UU 18 were slightly higher when compared to UU 17. The SiO_2 recovery in the tailings using UU 18 was the lowest among all three meaning it has the least selectivity for flotation of kaolinite. At a concentration of 400 g /ton, UU 13 exhibited the best performance regarding Al_2O_3 and SiO_2 grade and recovery. For this reason, the collector UU 13 was selected for further flotation experiments.

4.3.2 Customized Amine Effect on Reverse Flotation

Reverse flotation with and without desliming was performed after rod-mill grinding at 50% solids, with 80% of the product minus 113 microns. The experiments were performed in a 1L Denver cell at 1300 rpm. After pH adjustment and reagents

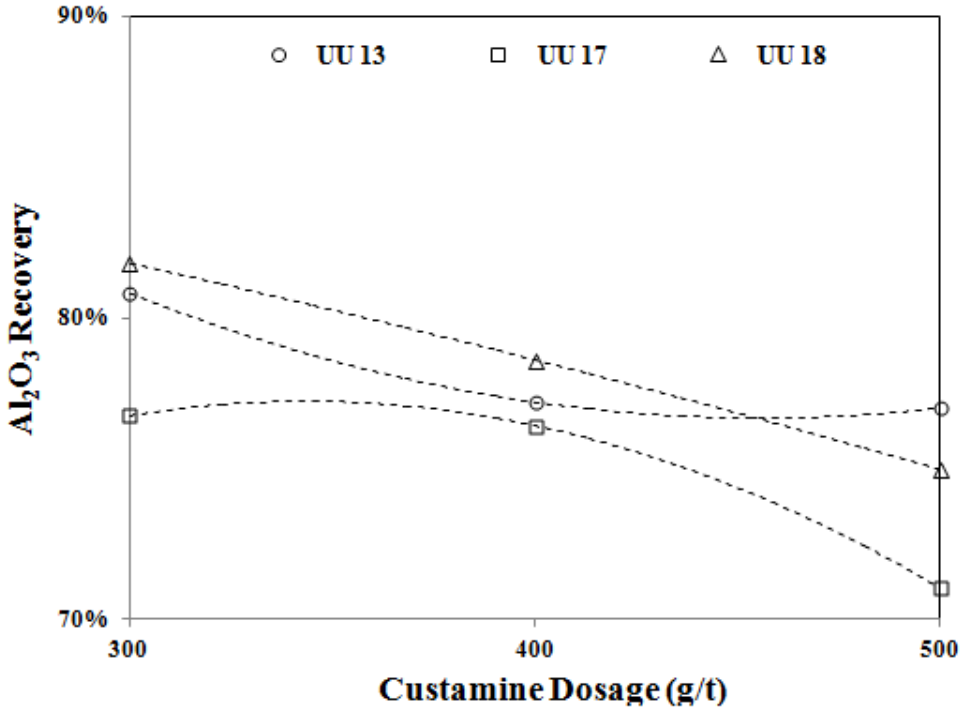

Figure 4.15. Effect of collector type on recovery in the concentrate for Al_2O_3, BNC bauxite ore (-150 microns), after one rougher and one scavenger stage at 25% solids, pH 4.

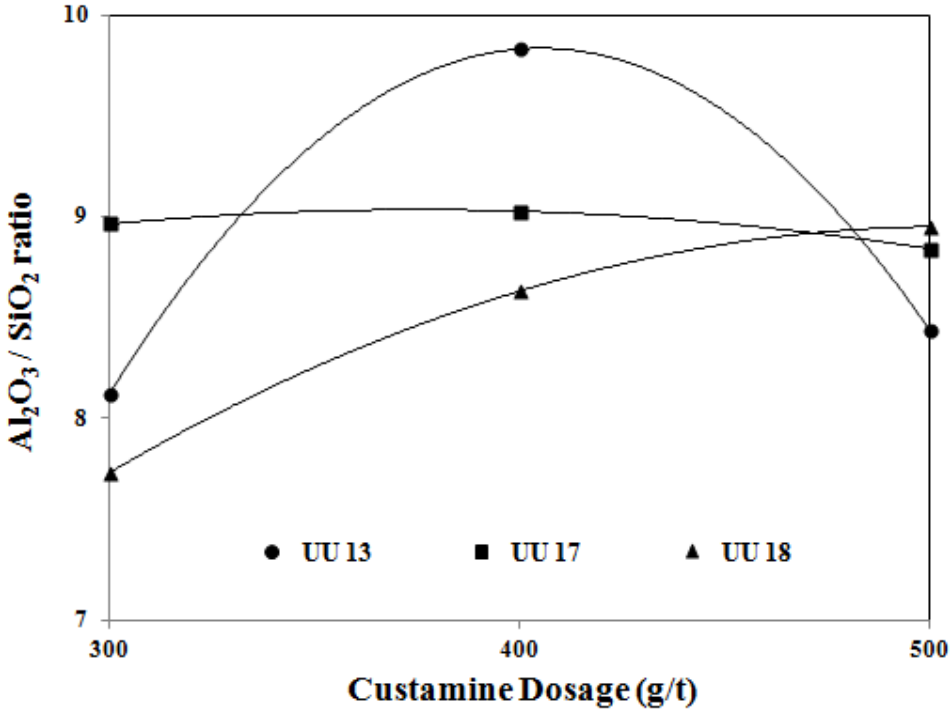

Figure 4.16. Effect of collector type on grade in the concentrate for Al_2O_3, BNC bauxite ore (-150 microns), after one rougher and one scavenger stage at 25% solids, pH 4.

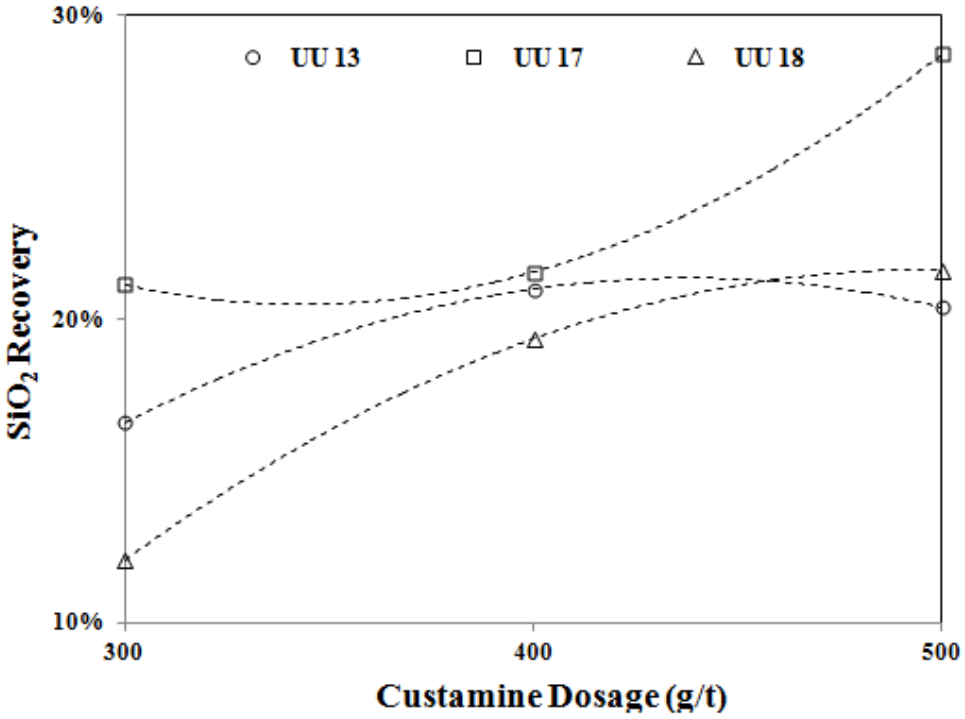

Figure 4.17. Effect of collector type on recovery in the concentrate for SiO_2, BNC bauxite ore (-150 microns), after one rougher and one scavenger at 25% solids, pH 4.

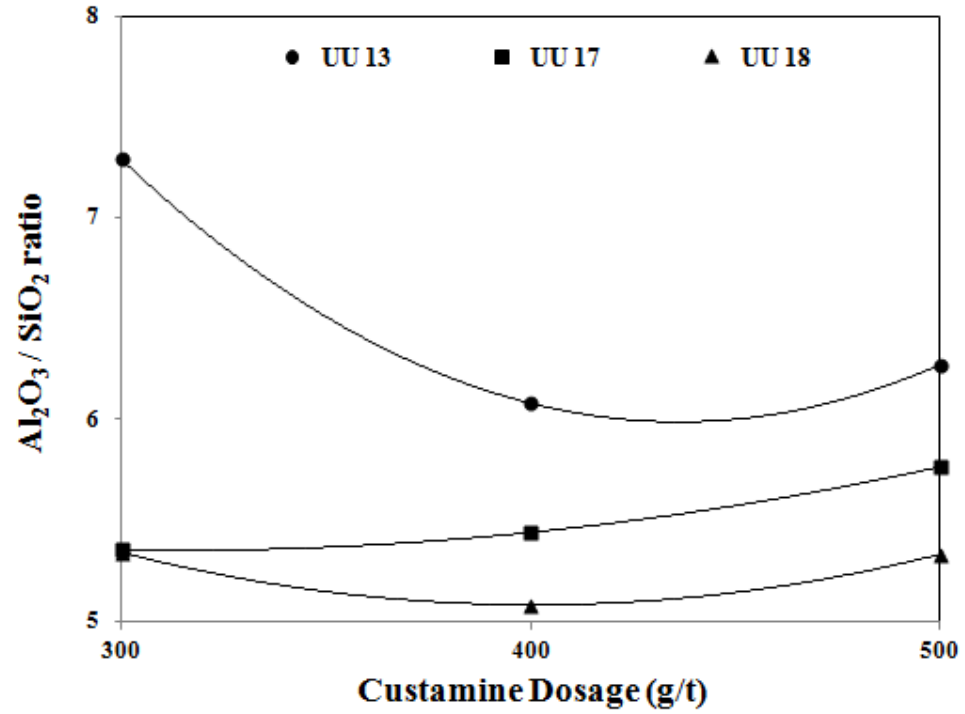

Figure 4.18. Effect of collector type on grade in the concentrate for SiO_2, BNC bauxite ore (-150 microns), after one rougher and one scavenger at 25% solids, pH 4.

addition, the conditioning time was 3 minutes. The rougher flotation stage was performed in 4 minutes and the scavenger or cleaner stage in 3 minutes. The effect of pH, dispersants, depressants and collector dosages was evaluated during the reverse flotation of kaolinite where the froth phase represents the kaolinite tailings. The amount of particles less than 400 mesh exceeded 50% by mass after rod-mill grinding and due to its high surface area. This condition plays an important role in the reagent adsorption phenomena.

Figures 4.19 and 4.20 exhibit the flotation response of BN bauxite ore and Figures 4.21 and 4.22 show the flotation response of the BNC bauxite ore with respect to collector dosage addition at pH 4.0 in the reverse flotation of kaolinite. For the flotation of the BN bauxite ore a maximum Al_2O_3 recovery of 57.3% was found at a concentration of 400 g / ton of the customized amine UU 13 while for the BNC bauxite ore, the collector dosage that maximized recovery at 80.8% was 300 g / ton using the same reagent. With respect to the product quality, the optimum performance for the BN bauxite ore occurred at a concentration slightly lower, 300 g / ton, with an Al_2O_3 grade of 51.1% and SiO_2 grade of 6.9% in the scavenger concentrate. In the case of BNC bauxite ore, at a concentration of 400 g / ton, the concentrate exhibited an Al_2O_3 grade of 57.1% and a SiO_2 grade of 5.81%. For both grade and recovery, the optimum collector dosage was found to be in the range of 300-400 g / ton at the rougher flotation stage independent of the ore type.

At a concentration higher than 400 g / ton, the tailings yield increased significantly for both bauxite ore types but as a consequence, the Al_2O_3 recovery in the concentrate decreased. For example, in the BN bauxite ore at 800 g / ton the yield

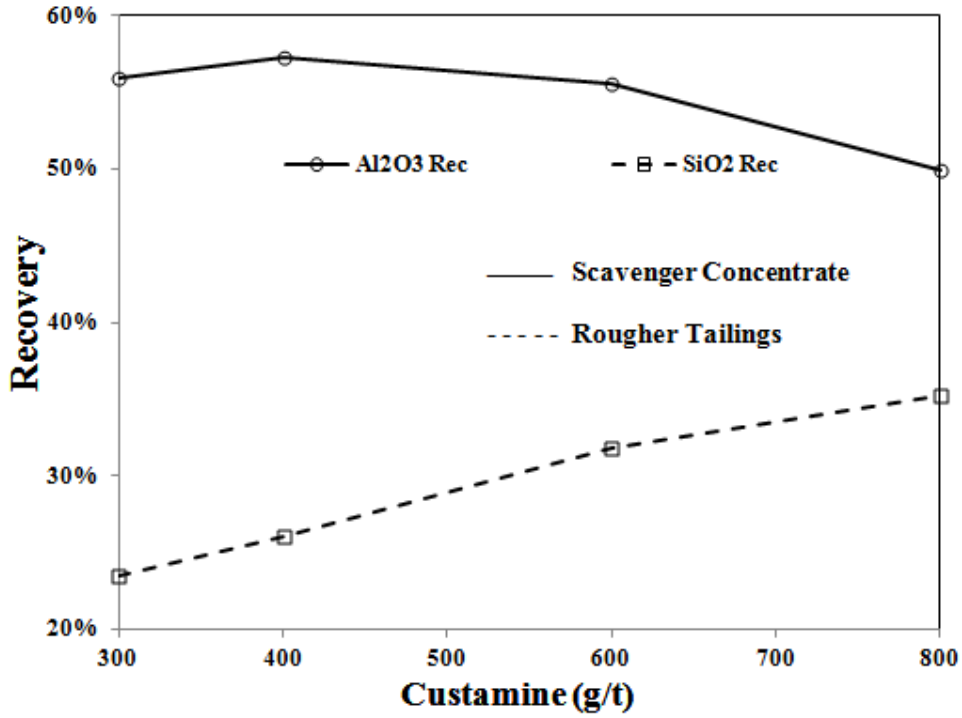

Figure 4.19 Effect of customized amine on recovery for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 4.

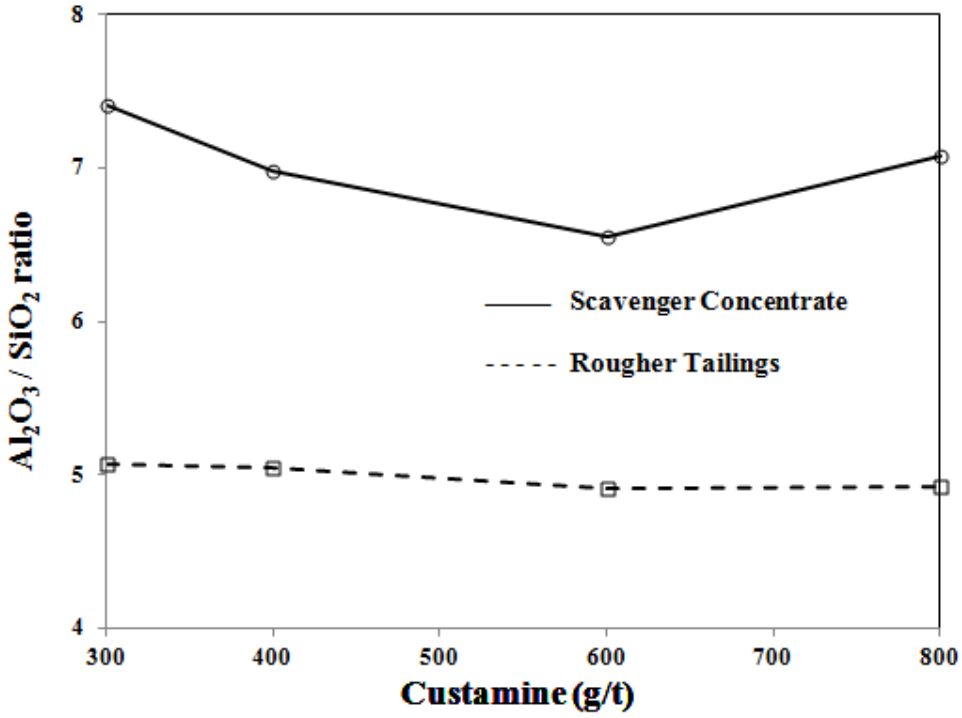

Figure 4.20 Effect of customized amine on grade for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 4.

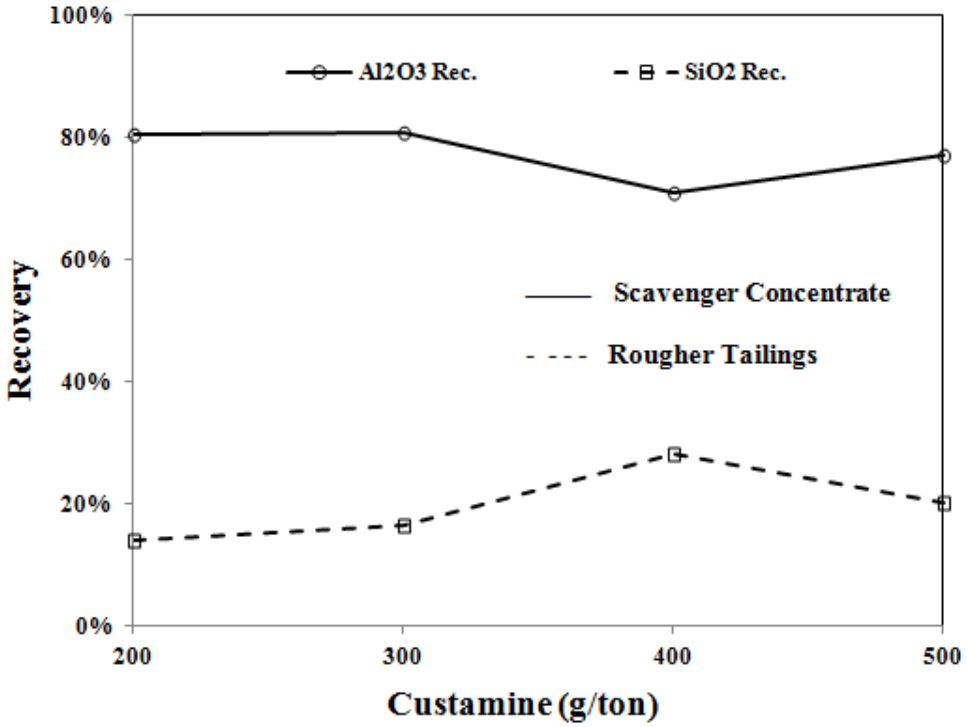

Figure 4.21 Effect of customized amine on recovery for reverse flotation without desliming with BNC bauxite ore, 80% passing 113 microns, pH 4.

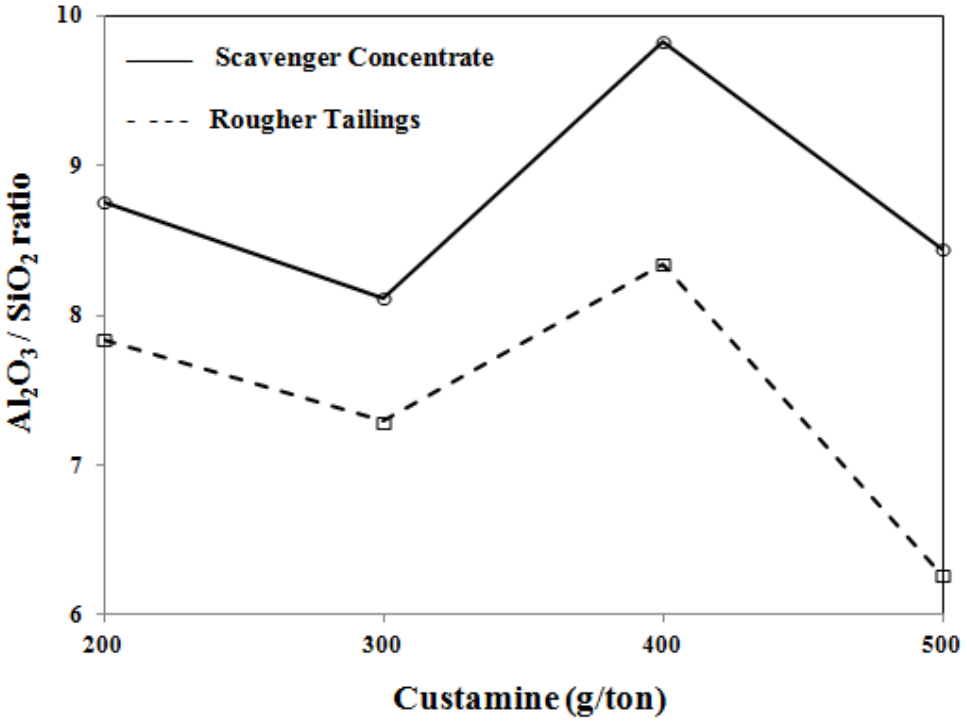

Figure 4.22 Effect of customized amine on grade for reverse flotation without desliming with BNC bauxite ore, 80% passing 113 microns, pH 4.

reaches 28% and the Al_2O_3 recovery drops to 49.9% while in the BNC bauxite ore at a 500 g / ton of custamine concentration, the tailings yield reaches 14% with 77% Al_2O_3 recovery. The concentration of 400 g / ton was considered for further evaluations of pH, dispersants and depressants during the research of reverse flotation of kaolinite for both ore types.

4.3.3 Effect of pH on Reverse Flotation

The pH effect on flotation response was evaluated during the reverse flotation of kaolinite where the surface charge differences between kaolinite and gibbsite play an important role in the collector adsorption mechanism. Figures 4.23 and 4.24 present the results from pH 2.0 to pH 10 using 400 g / ton of customized amine UU 13, 400 g / ton of starch, 1.5 kg / ton of SHMP and 25% solids. As expected, the highest selectivity level was achieved at pH lower than pH 6.0 where the recovery of SiO_2 in the tailings reached its maximum of 40% at pH 6.0 and dropped to 21.8% at pH 10. At pH 6.0 the rougher concentrate exhibited the Al_2O_3 grade of 5.86 after rougher flotation while the tailings SiO_2 grade was the same for all pH values higher than pH 4. At pH 8.0 and pH 10, the silica recovery in the concentrate is 77.3% and 78.2% resulting in a low Al_2O_3 to SiO_2 ratio of 5.49 and 5.33 respectively indicating a lower selectivity at higher pH values.

Since the surfaces of kaolinite and gibbsite are negatively charged at pH 10.0, the adsorption of the customized amine, UU 13, by kaolinite and gibbsite may occur and is probably the explanation for the lower quality of the concentrate. On the other hand, in the acidic region, pH < 6.0, the kaolinite alumina octahedral surface is positively charged and can adsorb amine by electrostatic attraction. In the acidic region, the amount of SiO2 reporting to the concentrate is lower than in the alkaline region, 60.1% against 78.2%.

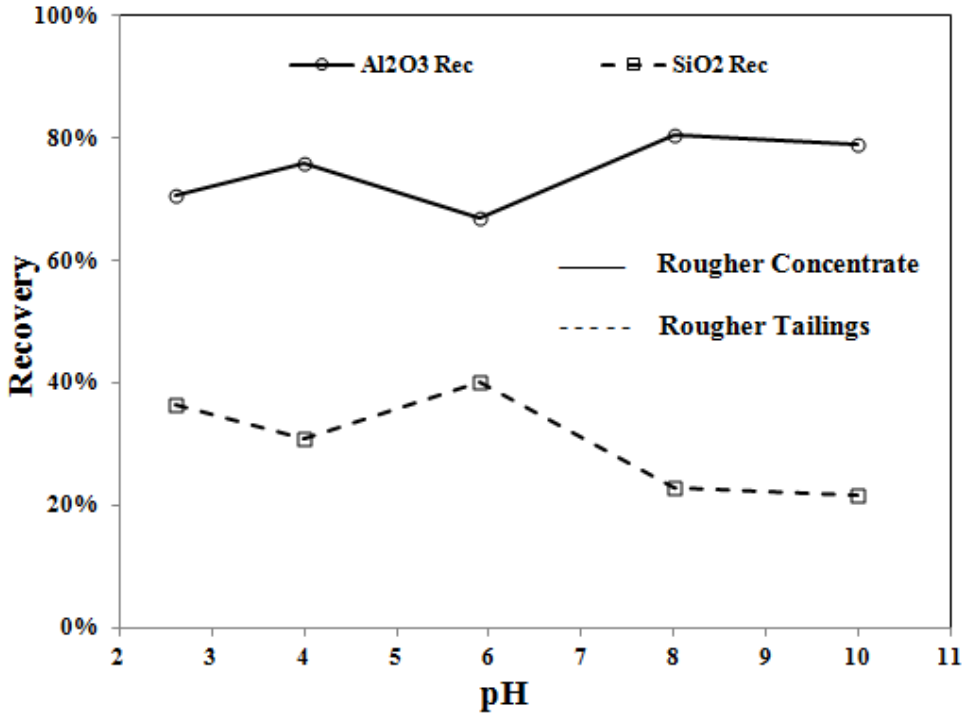

Figure 4.23 Effect of pH on recovery for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns.

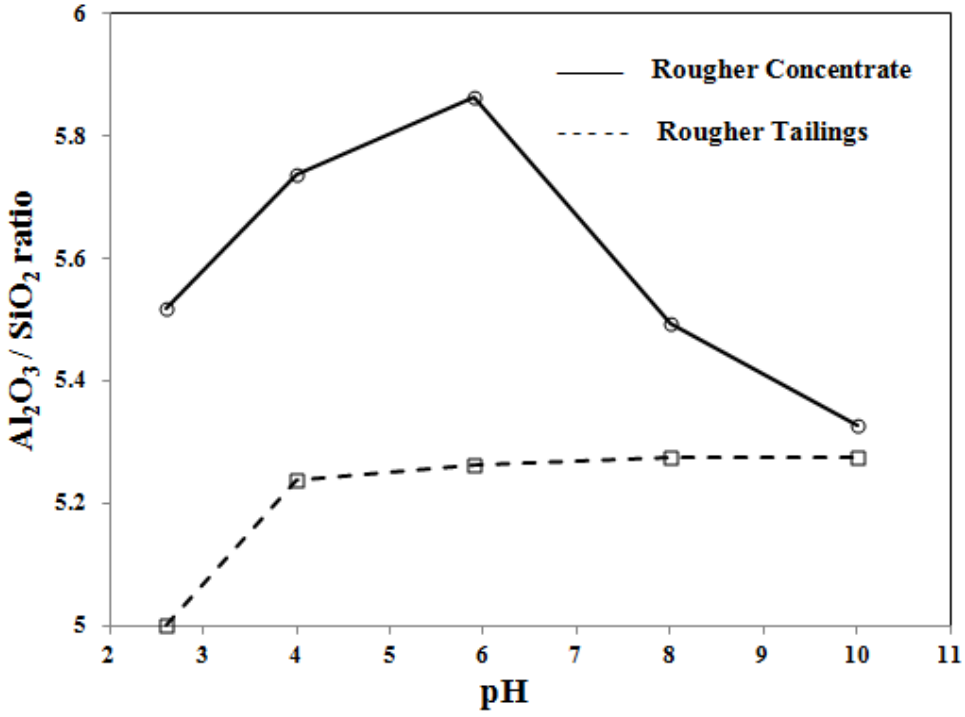

Figure 4.24 Effect of pH on grade for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns.

These results confirm the explanation of the anomalous behavior of kaolinite given by Gupta and Miller with respect to its surface charge (2010).

4.3.4 Effect of Sodium Hexametaphosphate on Reverse Flotation

The addition of sodium hexametaphosphate as a fine gibbsite dispersant is shown in Figures 4.25 and 4.26 using 400 g / ton of the customized amine and 500 g / ton of starch at pH 4.0 on the BN bauxite ore. It is clear that by increasing the SHMP dosage, the Al_2O_3 recovery in the concentrate increases until reaches a maximum of 78.2% at 2.25 kg / ton and drops to 63.5% at 3.0 kg / ton. Under the same conditions, the SiO_2 recovery in the concentrate increases with SHMP addition until a dosage of 2.25 kg / ton reaching 71.7%. At a concentration of 3.0 kg / ton, the SiO_2 recovery in the concentrate decreases to 55.4% although it is the SHMP dosage with the highest Al_2O_3 to SiO_2 ratio of 5.96. The optimum dispersant dosage which maximizes recovery at 78.2% is 2.25 kg / ton. In terms of grade, at a SHMP dosage of 3.0 kg / ton the concentrate presents the highest selectivity with Al_2O_3 to SiO_2 ratio of 5.96 in the rougher concentrate and 45% of SiO_2 recovery in the silica rougher tailings. Due to the high amount of fines less than 45 microns, a higher SHMP dosage was necessary to achieve the desired separation efficiency.

4.3.5 Effect of Starch on Reverse Flotation

The starch addition as a depressant for the oxide minerals during the reverse flotation of kaolinite is shown in Figures 4.27 and 4.28 where 400 kg / ton of the customized amine UU 13 and 1.5 kg / ton SHMP was used.

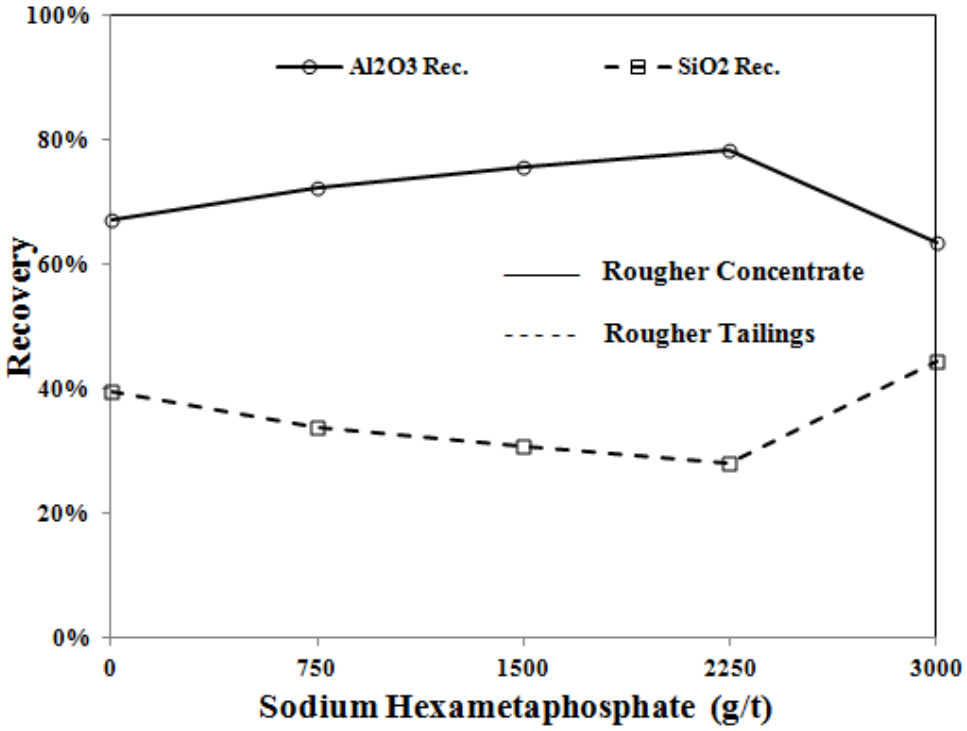

Figure 4.25 Effect of sodium hexametaphosphate on recovery for reverse flotation without desliming for the BN bauxite ore, 80% passing 113 microns, pH 4.

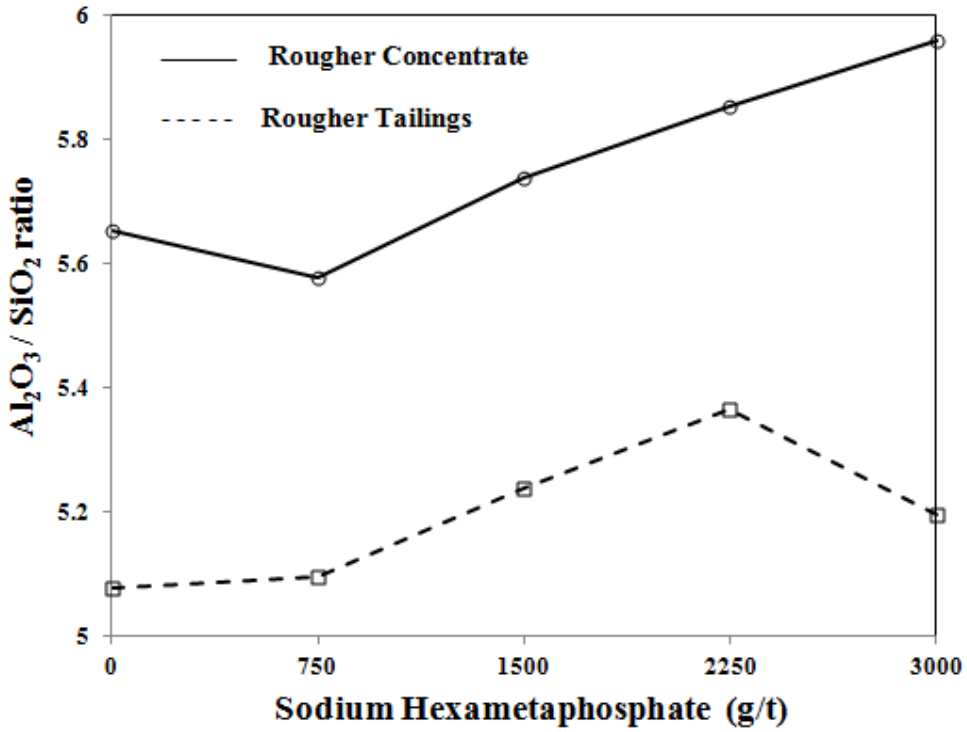

Figure 4.26 Effect of sodium hexametaphosphate on grade for reverse flotation without desliming for the BN bauxite ore, 80% passing 113 microns, pH 4.

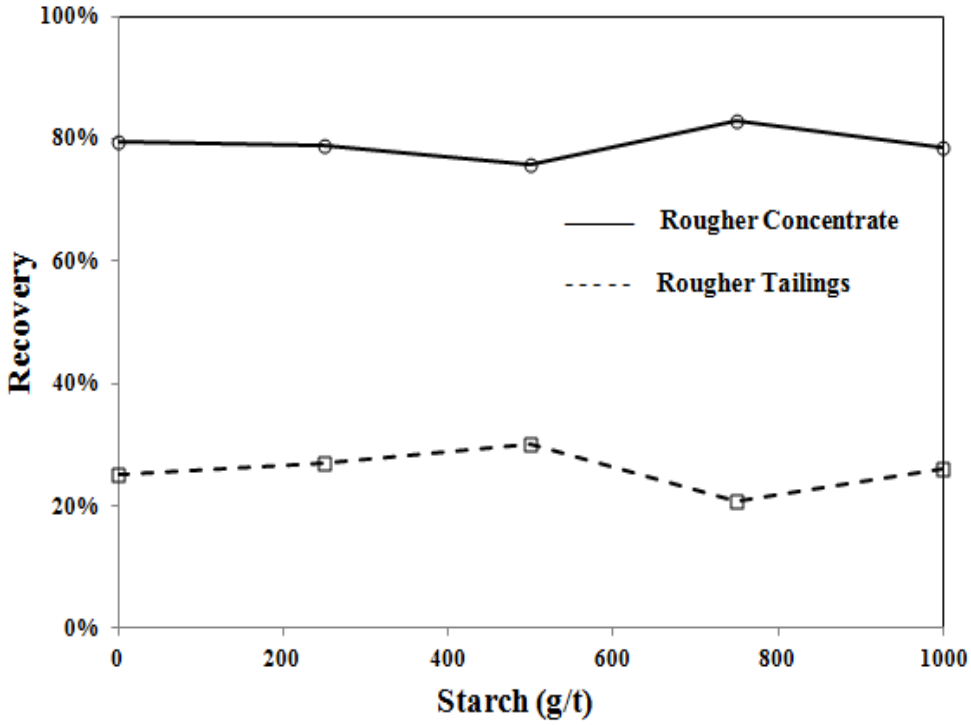

Figure 4.27 Effect of starch on recovery for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 4.

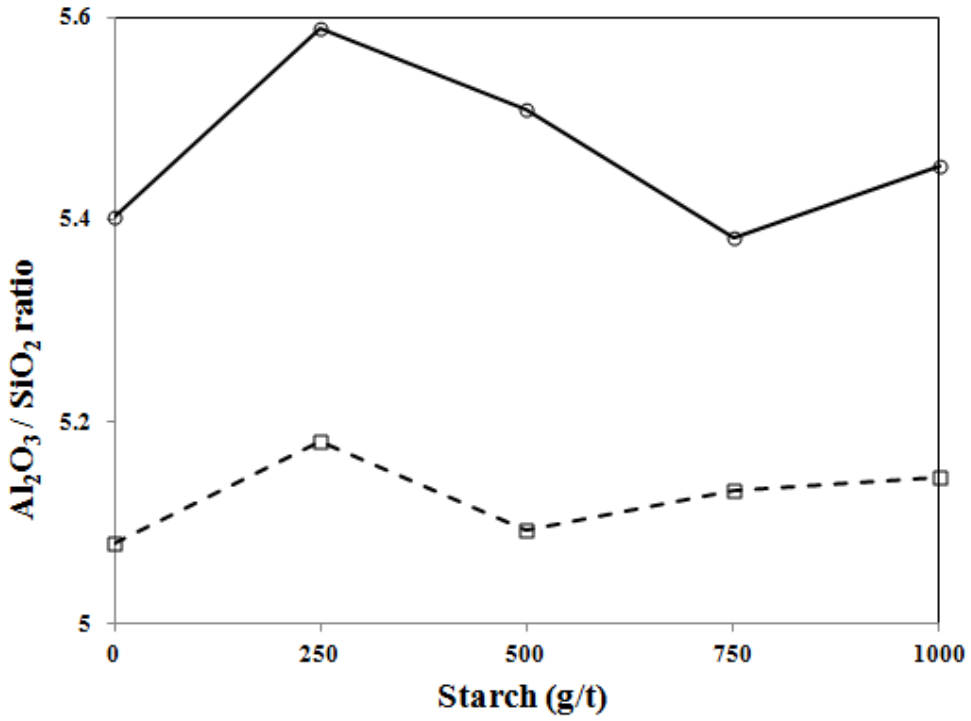

Figure 4.28 Effect of starch on grade for reverse flotation without desliming with BN bauxite ore, 80% passing 113 microns, pH 4.

At a concentration of 750 g / ton of starch the concentrate Al_2O_3 recovery is 83% but the SiO_2 recovery shows a maximum of 79.2% in the concentrate. At a 500 g / ton starch dosage, the concentrate quality exhibits an Al_2O_3 to SiO_2 ratio of 5.51 but with the SiO_2 recovery in the concentrate the lowest, 70.0%. Higher starch concentration results in higher iron oxide depression which frequently is associated with aluminum oxide.

4.3.6 Effect of the Customized Amine on Flotation With Desliming

Flotation with desliming was conducted by removing particles less than 38 microns for the BN bauxite ore and less than 15 microns after rod-mill grinding for the BNC bauxite ore, since the BN bauxite ore presents a higher concentration of kaolinite in the fine particle size range. After pH adjustment and reagent addition, the conditioning time was 3 minutes. The rougher flotation stage was performed in 4 minutes and scavenger stage in 3 minutes.

The customized amine effect was examined on BN and BNC bauxite ores by one rougher flotation stage followed by one scavenger stage. Results from reverse flotation are shown in Figures 4.29 through 4.32 and reveal similar behavior between the two bauxite ores regarding flotation response. For the experiments, 0.4 kg / ton and 0.5 kg / ton of starch and 0.15 g / ton and 0.1 kg / ton of SHMP for BN and BNC bauxite ores were used respectively. In the BN bauxite ore, as the collector dosage increased from 200 to 400 g / ton, the tailings yield also increased from 10.1% to 15.7% respectively and the Al_2O_3 recovery in the concentrate decreased from 73.5% to 61.3%. The scavenger concentrate quality reaches its maximum at the concentration of 400 g / ton, with an Al_2O_3 to SiO_2 ratio of 6.07.

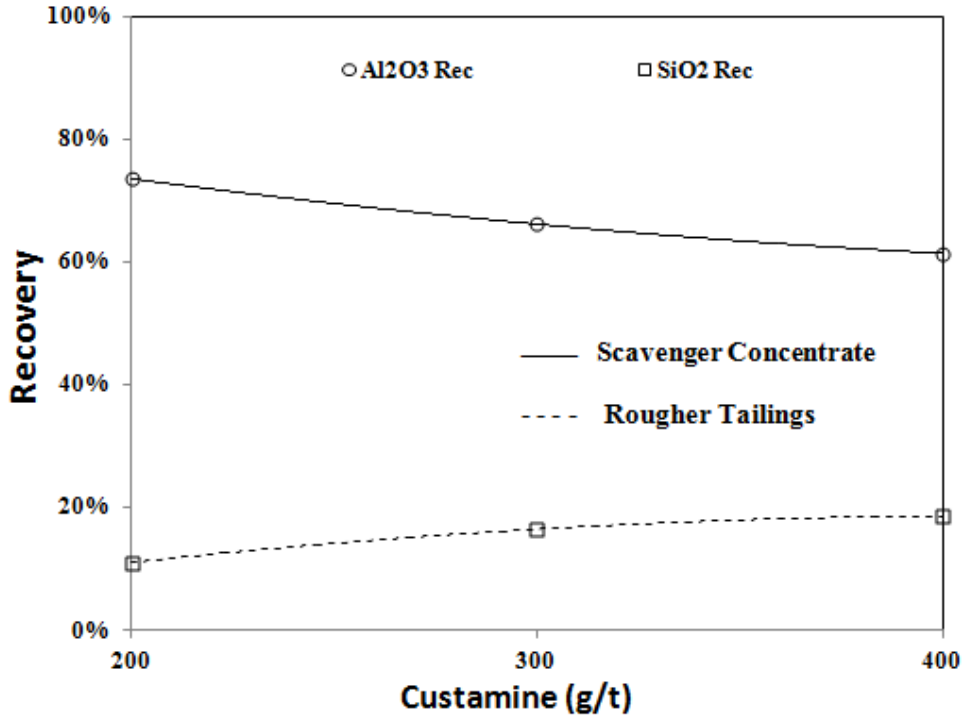

Figure 4.29 Effect of desliming on recovery for reverse flotation with BN bauxite ore, 80% passing 113 microns, pH 4.

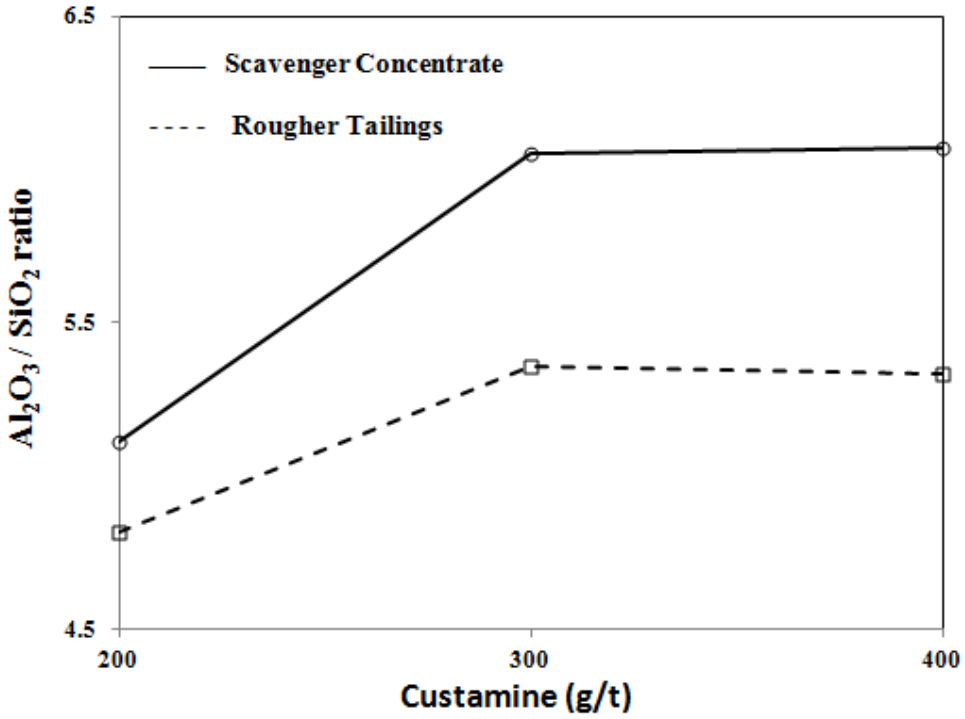

Figure 4.30 Effect of desliming on grade for reverse flotation with BN bauxite ore, 80% passing 113 microns, pH 4.

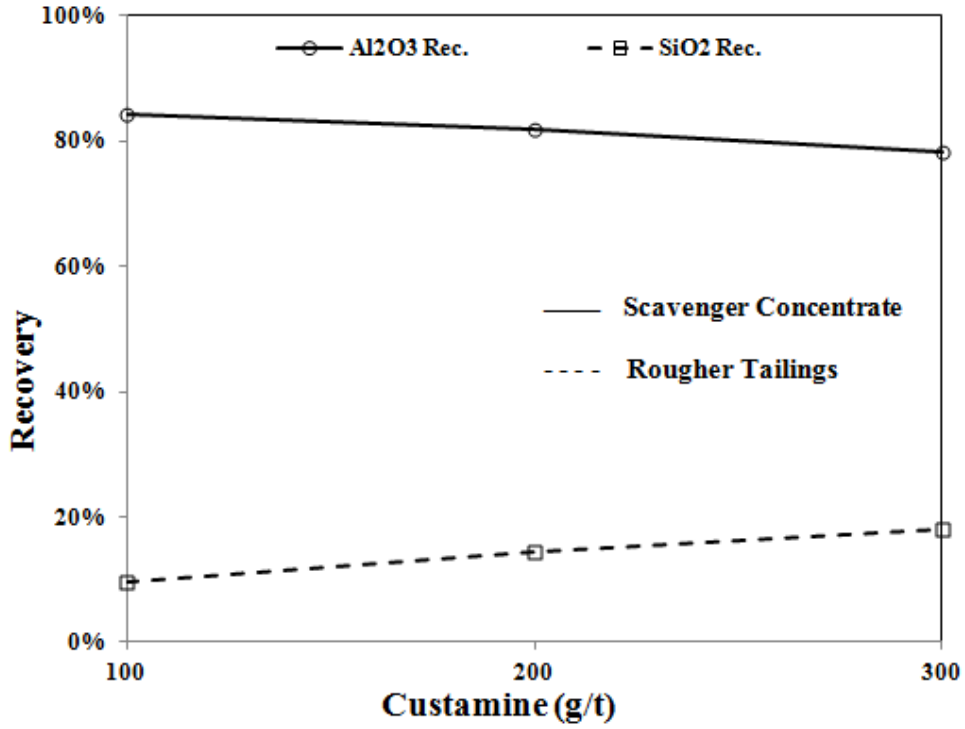

Figure 4.31 Effect of desliming on recovery for reverse flotation with BNC bauxite ore, 80% passing 113 microns, pH 4.

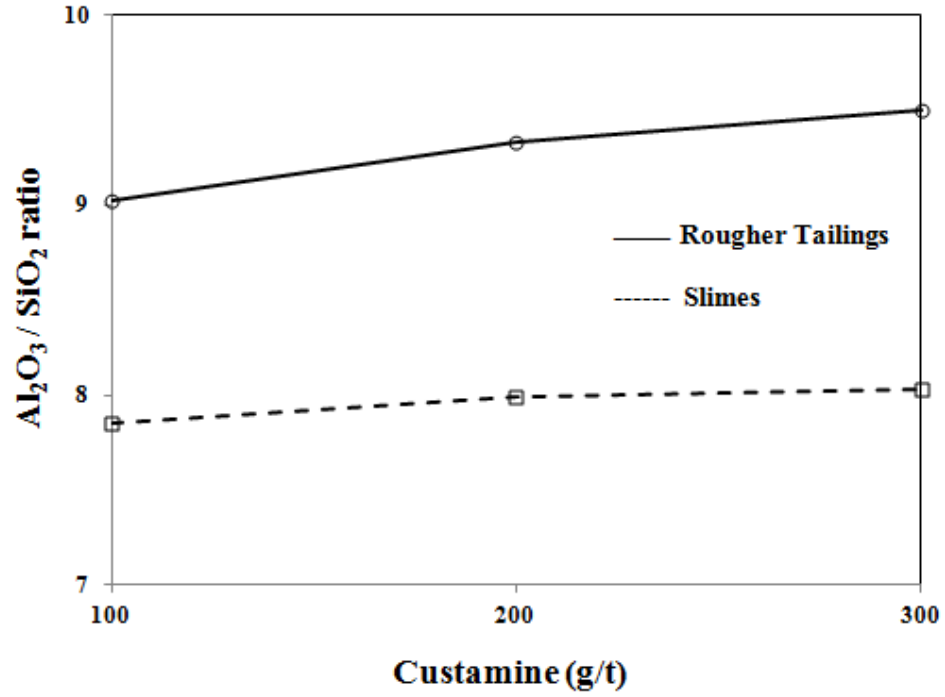

Figure 4.32 Effect of desliming on grade for reverse flotation with BNC bauxite ore, 80% passing 113 microns, pH 4.

For the BNC bauxite ore, the maximum recovery of 84.3% was achieved using 100 g / ton while the maximum Al_2O_3 to SiO_2 ratio of 9.50 in the concentrate was achieved when 300 g / ton was added to the rougher flotation stage. Once again, at low collector concentration the concentrate exhibits a higher Al_2O_3 recovery while at increasing collector dosage, the Al_2O_3 grade increases.

4.3.7 Summary for Reverse Flotation

Based on the results from the effects of collector, dispersant, depressant and pH on reverse flotation, a particular flotation strategy process was established to achieve the specifications of Bayer process feed material. The addition of subsequent scavenger flotation after rougher flotation of kaolinite was introduced.

Reverse flotation of kaolinite was accomplished, with and without desliming, for both BN and BNC bauxite ores using a customized amine with better results in the acidic region, pH < 6.0 in the rougher and scavenger flotation stages. The collector dosage range was found to be 300 – 400 g / ton, depressant 400 – 500 g / ton and dispersant 1.5 kg / ton. Desliming the flotation feed increased Al_2O_3 recovery and reduced collector addition but significantly decreased the Al_2O_3 to SiO_2 ratio in the concentrate.

Tables 4.9 and 4.10 show the flotation performance for the reverse flotation of kaolinite for the BN and BNC bauxite ores. The Al_2O_3 to SiO_2 ratios in the concentrate were found to be 7.41 and 9.83 respectively. On the other hand, the Al_2O_3 recovery in the concentrate was found to be 55.9% and 70.9% for BN and BNC respectively where for the direct flotation recoveries were 32.0% and 65.8% for BN and BNC. The overall losses in recovery due to desliming are also revealed by the slimes quality.

Table 4.9 Reverse flotation of kaolinite of BN bauxite ore without desliming at pH 4.0, with 0.3 kg / ton customized amine UU 13, 1.5 kg / ton sodium hexametaphosphate and 0.4 kg / ton starch after one rougher and two scavenger flotation stages.

	Yield %	Grade		Recovery		Al_2O_3/SiO_2
		Al_2O_3	SiO_2	Al_2O_3	SiO_2	
Al_2O_3 Concentrate	53.1	51.1	6.9	55.9	41.1	7.41
Middlings 1	20.6	45.2	11.3	19.2	26.2	6.08
Middlings 2	7.4	45.3	11.2	6.9	9.3	5.83
SiO_2 Tailings	18.8	46.2	11.1	17.9	23.4	5.06
Feed	100	48.5	8.9	100	100	5.44

Table 4.10 Reverse flotation of kaolinite of BNC bauxite ore without desliming at pH 4.0, with 0.4 kg / ton customized amine UU 13, 1.5 kg / ton sodium hexametaphosphate and 0.5 kg / ton starch after one rougher and one scavenger flotation stage.

	Yield %	Grade		Recovery		Al_2O_3/SiO_2
		Al_2O_3	SiO_2	Al_2O_3	SiO_2	
Al_2O_3 Concentrate	69.3	57.1	5.8	70.9	60.2	9.83
Middlings	9.5	54.7	8.1	9.4	11.5	9.34
SiO_2 Tailings	21.2	51.9	8.9	19.7	28.3	8.34
Feed	100	55.8	6.7	100	100	8.34

While the SiO_2 recovery in the tailings is generally higher than in the slimes, the Al_2O_3 recovery in the tailings is also higher than in the slimes. Since the particles containing kaolinite and gibbsite in the coarser range can be adsorbed by the collector and the desliming removes the fine particle size fraction (less than 400 mesh), the final result in terms of removing the gangue will be similar. The advantage of desliming is that no collector is added during the removal of fines but desliming may also remove the fine gibbsite particles resulting in the overall lower recoveries. On the other hand, when using higher dosages of collector, recoveries are higher but it may float more particles containing kaolinite and will require more scavenger stages to reach the desired grade.

4.4 Liberation Analysis

The beneficiation of low grade bauxite ores requires appropriate technology, and consequently the understanding of the liberation characteristics of the minerals presented in the bauxite is extremely important. Samples from the concentrate and tailings after flotation with and without desliming were taken for liberation analysis by QEMSCAN. The concentrate was divided into eight size fractions while the tailings and the slimes were used as a composite.

4.4.1 Effect of Particle Size on Direct Flotation

Also important to notice is the effect of flotation feed particle size during the direct flotation of gibbsite. If the flotation feed is too coarse, the overall flotation may be affected by the hydrodynamics in the flotation system. On the other hand, if the particle size of the flotation feed is very fine, the flotation efficiency will also be affected by hydrodynamics.

Table 4.11 Effect of flotation feed particle size distribution on the direct flotation of gibbsite using 3.0 kg / ton of alkyl hydroxamate, 2.0 kg / ton sodium silicate and 3.0 kg / ton sodium carbonate in the rougher stage at pH 10.5.

	80% < 200 mesh	**90% < 200 mesh**	**100% < 200 mesh**
Al_2O_3 Concentrate			
Al_2O_3 Grade	55.5	55.0	56.2
Al_2O_3 Recovery	73.7	77.2	71.9
SiO_2 Tailings			
SiO_2 Grade	12.0	12.0	10.1
SiO_2 Recovery	13.1	7.3	18.1

Liberation of the gibbsite grains suggests that at a particle size fraction 106, 70% of the particles contain more than 50% gibbsite. In this regard, some experiments of the direct flotation of gibbsite were done to evaluate the effect of flotation feed particle size on the flotation response as shown in Table 4.11. For the concentrate, maximum Al_2O_3 recovery was found in an intermediate level, 90% < 200 mesh but also the silica recovery in the tailings was very low, only 7.3%. The finer flotation feed reported the lowest Al_2O_3 recovery in the concentrate, 71.9% indicating that the amount of fines is harmful for a selective flotation of gibbsite. In the coarser flotation, the Al_2O_3 in the concentrate was also low, 73.7%.

4.4.2 Liberation Characteristics of BNC Bauxite Ore

The flotation feed (80% minus 113 microns) was sampled with a rotary sampler divider and prepared for QEMSCAN® analysis as described previously. The polished sections were analyzed for the major mineral constituents and classified into four groups: aluminum oxides (gibbsite and boehmite), clay minerals (kaolinite, pyrophyllite and illite), hematite, and quartz. Each particle section was analyzed with respect to aluminum oxide content and clay content. The results were classified according to composition and organized into either an aluminum oxide group or clay mineral group as shown in Figure 4.33 for the BNC bauxite ore.

The aluminum oxide minerals exhibit a greater degree of liberation than the clay minerals. For example, in the case of BNC bauxite ore more than 50% of the aluminum oxide minerals are found in particles with a composition exceeding 70% in the flotation feed, which means that for particles exceeding 70% in aluminum oxide the extent of

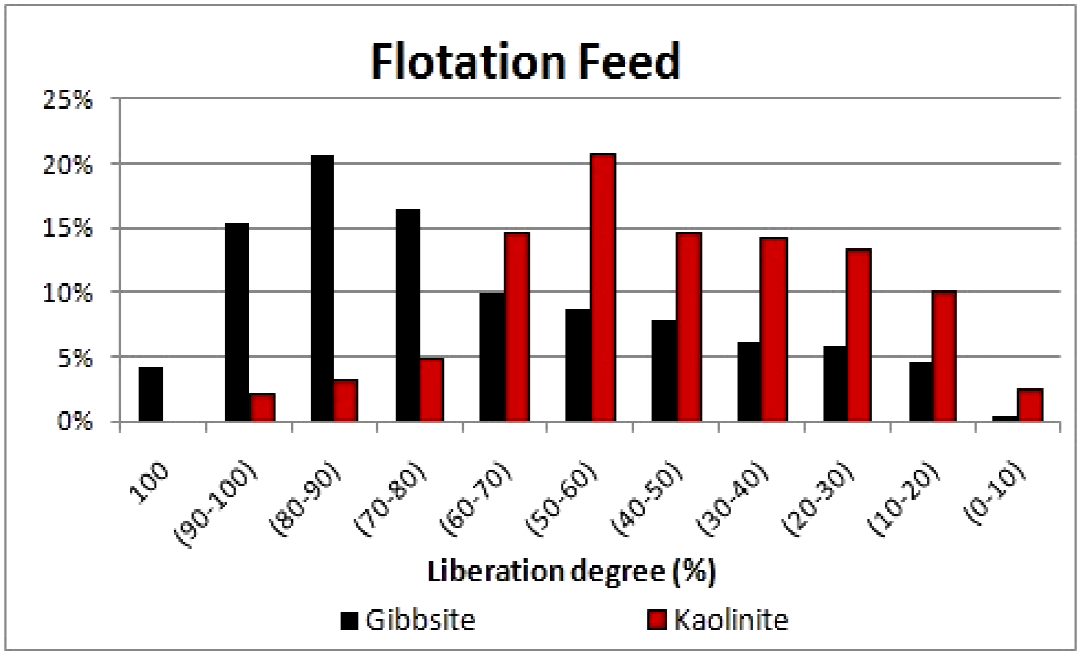

Figure 4.33 Liberation degrees of gibbsite and kaolinite for BNC bauxite ore, 80% minus 113 microns.

liberation is greater than 50%. In contrast, the clay minerals are not so well liberated. Only 8% of the clay minerals are found in particles containing more than 70% of clay. Most of the clay minerals are found in particles that contain less than 50% clay. The feed distribution also has fines less than 10 microns that may be associated with iron oxide minerals such as hematite. The flotation products from reverse flotation, concentrate and tailings, were also analyzed by QEMSCAN and revealed for the bauxite concentrate a small presence of kaolinite particles as a non liberated mineral phase in the gibbsite matrix. This may be explained by the accommodation of clay minerals with a very small grain size at the gibbsite and hematite surfaces accounting for the adsorption of collector. On the other hand, the tailings froth product from reverse flotation reveals the presence of gibbsite particles as a mixture with clays and iron oxides. Figure 4.34 shows the distribution of aluminum oxide and clay minerals in the concentrate. The aluminum oxide particles are green while the clay minerals are blue.

The aluminum oxide concentrate product contains mostly liberated aluminum oxide particles but also carries some clay mineral particles. The presence of hematite in the aluminum oxide concentrate is not significant which indicates that these minerals are being floated with kaolinite.

Figure 4.35 shows the distribution of aluminum oxide and clay mineral particles in the silica froth phase product for the BNC bauxite ore. A significant presence of clay minerals is identified but the presence of aluminum oxide can be seen due to the non-liberated status of these particles. The aluminum oxide particles are green particle sections while the clay minerals are blue. For reverse flotation (removal of quartz and silica gangue minerals in the froth phase), the effectiveness of the experiment is not

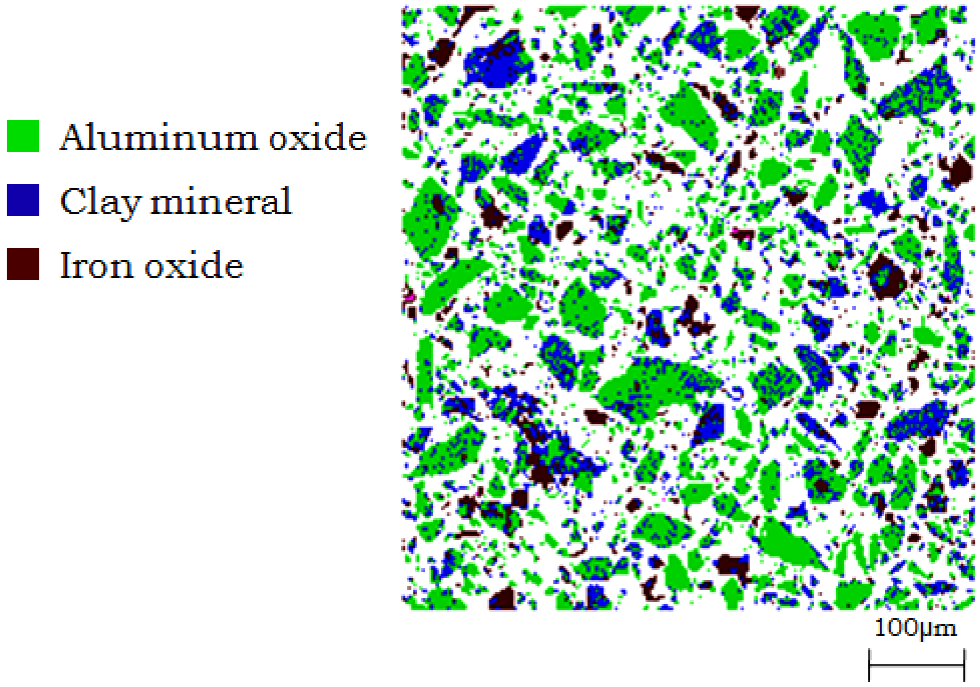

Figure 4.34 Distribution of aluminum oxide particles (gibbsite – green), clay minerals (kaolinite – blue) and iron oxide (hematite – brown) in the scavenger concentrate for reverse flotation at pH 4.0 and 400 g / ton of the customized amine for BNC bauxite ore.

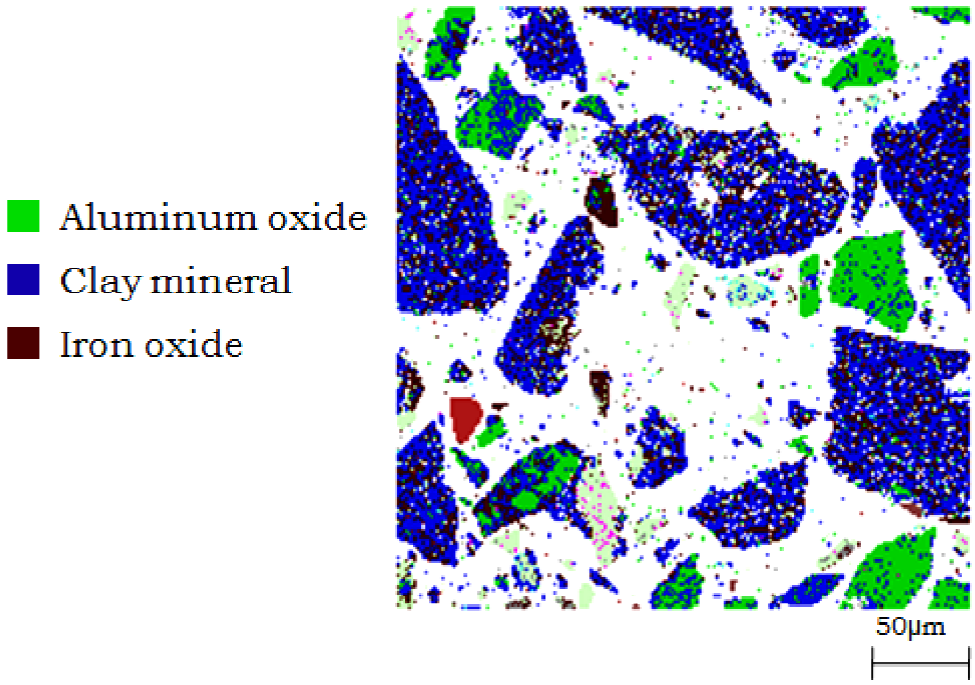

Figure 4.35 Distribution of aluminum oxide particles (gibbsite – green), clay minerals (kaolinite – blue) and iron oxide (hematite – brown) in the rougher tailings for reverse flotation at pH 4.0 and 400 g / ton of the customized amine for BNC bauxite ore.

maximized due to the presence of a significant amount of clay mineral particles in the aluminum oxide concentrate. This observation is also confirmed by the presence of a small amount of aluminum oxide particles reporting to the froth since it was floated with the silica gangue. The presence of hematite and quartz is also observed in the tailings.

The QEMSCAN liberation analysis of the reverse flotation products (alumina concentrate and silica tailings) also provides more evidence to support the flotation strategy considered. In the concentrate, almost 90% of the aluminum oxide particles are found with a composition exceeding 50% while all clay mineral particles have a composition of approximately 30%. In contrast, the composition of clay mineral particles in the tailings was found to be in the range of 50-60% while the aluminum oxide particles generally no more than 20%.

CHAPTER 5

DISCUSSION AND CONCLUSIONS

The flotation of marginal bauxite ores from the Paragominas deposit, Bazil, was successfully accomplished for both BN and BNC bauxite ores through direct flotation of gibbsite and reverse flotation of kaolinite. The most important advantage as compared to the current desliming process is the higher metallurgical recovery and the possibility of considering marginal ores for processing in the plant. Flotation parameters can be adjusted depending on the feed quality and the need to realize high selectivity especially when treating very fine particles.

Different flotation strategies, direct and reverse, can be applied with pros and cons for both strategies. While direct flotation of gibbsite appears to be more efficient with respect to the concentrate grade, flotation of kaolinite by reverse flotation is more effective regarding the metallurgical recovery. The flotation of gibbsite using alkyl hydroxamate required desliming prior to flotation contributing to the lower recoveries. On the other hand, reverse flotation of kaolinite from these bauxite ores was efficient without desliming confirming that special customized amines can be effective in floating very fine kaolinite particles from gibbsitic bauxite ores.

The electrostatic adsorption of a cationic collector such as amine by kaolinite under acidic conditions is expected to be primarily at the silica face, which has its PZC at pH 4.0. It is also expected that at low pH values, the aggregation of kaolinite particles

may contribute to the exposure of the silica face to the amine. During the flotation of gibbsite, the adsorption mechanism of hydroxamate by gibbsite may be related to chemical bonding or chemisorption at pH 10.5 under which conditions flotation was found to be less selective when compared to reverse flotation with amines. At high pH levels, both kaolinite and gibbsite are negatively charged.

Liberation analysis revealed the major concentration of kaolinite the fine size fraction, < 400 mesh, and in addition, kaolinite was found to be finely dispersed in the gibbsite matrix. Kaolinite was found to be generally associated with hematite and anatase. Gibbsite particles were estimated to have an average grain size of 75 microns for both BN and BNC bauxite ores. However grinding the ore to this size generates a substantial amount of fines and would be harmful to flotation efficiency. For a coarser grind, the alumina recovery is higher but the concentrate contains a significant amount of kaolinite which is not well liberated. There are two options for the Paragominas plant to accommodate the processing of low grade marginal bauxite ores: The first is blending the BN and BNC bauxite ores and homogenizing for feed to the flotation plant. The result would be a higher Al_2O_3 content and the effect on overall recovery diminished. The second option is to consider the underflow of the first and second desliming stages as feed for flotation. Particles less than 15 and 45 microns are removed during desliming by cyclones and can be accommodated into the flotation design as shown in this thesis research. The economic balance between grade and recovery is a major issue which must be considered as flotation technology for the processing and recovery of aluminum minerals from bauxite ores continues to evolve.

APPENDIX

TABULATION OF DATA USED IN FIGURES

Table A.1

Data for Figure 4.3 and 4.4

UU 13 ($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
300	55.20	80.80	10.50	16.60
400	55.20	77.20	10.20	21.00
500	53.70	77.00	10.20	20.40

UU 17 ($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
300	54.85	76.75	9.82	21.14
400	54.70	76.42	9.74	21.56
500	54.91	71.05	9.19	28.72

UU 18 ($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
300	54.80	81.80	9.84	12.08
400	54.40	78.60	10.50	19.36
500	54.80	74.97	9.84	21.62

Table A.2

Data for Figure 4.5

UU 13	Rougher Concentrate		Rougher Tailings	
(gton^{-1})	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
200	55.00	80.66	9.68	14.11
300	55.20	80.77	10.50	16.58
400	57.10	70.94	8.92	28.26
500	53.70	77.01	10.20	20.36

Table A.3

Data for Figure 4.6

UU 13	Scavenger Concentrate		Rougher Tailings	
(gton^{-1})	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
300	51.10	55.90	11.10	23.45
400	49.40	57.30	12.10	26.00
600	48.70	55.54	11.90	31.81
800	49.40	49.88	12.00	35.18

Table A.4

Data for Figure 4.7

XD 903	Scavenger Concentrate		Rougher Tailings	
($gton^{-1}$)	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
2000	58.20	72.90	9.71	22.38
2500	57.30	78.37	9.88	23.43
3000	55.50	73.65	12.00	13.01

Table A.5

Data for Figure 4.8

XD 903	Scavenger Concentrate		Rougher Tailings	
($gton^{-1}$)	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
1500	49.40	50.17	9.18	50.70
2250	48.90	59.11	9.00	40.80
3000	48.80	62.75	8.99	36.70

Table A.6

Data for Figure 4.9

pH	Rougher Concentrate		Rougher Tailings	
	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
2.6	47.90	70.62	11.30	36.31
4.0	48.60	75.81	11.10	30.78
6.0	48.90	67.00	10.60	40.01
8.0	48.30	80.48	10.20	22.74
10.0	48.00	79.00	9.45	21.76

Table A.7

Data for Figure 4.10

SHMP	Rougher Concentrate		Rougher Tailings	
($gton^{-1}$)	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
0.0	48.50	67.21	10.90	39.63
750	48.30	72.43	11.00	33.82
1500	48.60	75.81	11.11	30.78
2250	48.40	78.25	11.02	28.27
3000	49.02	63.50	10.80	44.60

Table A.8

Data for Figure 4.11

Starch	**Rougher Concentrate**		**Rougher Tailings**	
($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
0.0	48.30	79.46	11.10	25.29
250	48.40	78.85	11.08	26.91
500	48.20	75.68	11.07	30.02
750	47.80	83.02	11.01	20.84
1000	48.10	78.43	10.81	26.01

Table A.9

Data for Figure 4.12

Na_2CO_3	**Rougher Concentrate**		**Rougher Tailings**	
($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
0.0	49.10	60.79	9.76	42.26
2000	49.80	60.85	9.23	42.21
4000	48.6	62.95	9.86	38.94
6000	48.90	59.11	9.48	40.80
8000	49.20	62.91	8.57	36.15

Table A.10

Data for Figure 4.13

NaSi	Rougher Concentrate		Rougher Tailings	
(gton^{-1})	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
0.0	49.10	58.93	8.83	40.26
250	49.20	60.48	8.95	40.15
500	48.50	62.52	8.75	36.35
750	48.90	59.11	9.00	40.80
1000	48.50	63.63	9.18	36.63

Table A.11

Data for Figure 4.14

UU 13	Scavenger Concentrate		Rougher Tailings	
(gton^{-1})	Al_2O_3 Grade	Al_2O_3 Rec.	SiO_2 Grade	SiO_2 Rec.
100	56.70	84.28	9.91	9.48
200	56.30	81.78	10.20	14.30
300	57.01	78.34	9.83	18.08

Table A.12

Data for Figure 4.15

UU 13	**Scavenger Concentrate**		**Rougher Tailings**	
($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
100	47.40	73.50	11.20	11.01
200	48.90	66.11	11.31	16.41
300	48.70	61.33	11.02	18.60

Table A.13

Data for Figure 4.16

XD 903	**Scavenger Concentrate**		**Rougher Tailings**	
($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
1000	58.30	64.46	8.81	32.78
1500	57.50	67.61	7.89	28.07
2000	57.52	71.22	8.31	26.46
2500	57.48	72.73	8.15	22.69

Table A.14

Data for Figure 4.17

XD 903	**Scavenger Concentrate**		**Rougher Tailings**	
($gton^{-1}$)	**Al_2O_3 Grade**	**Al_2O_3 Rec.**	**SiO_2 Grade**	**SiO_2 Rec.**
1250	54.30	32.02	10.60	45.33
1800	51.02	52.22	9.90	27.19
2500	50.98	51.11	10.70	23.65

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